

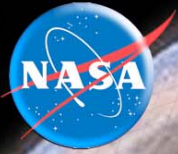


Precise Heat Control: What Every Scientist Needs to Know About Pyrolytic Techniques to Solve Real Problems

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ES4 Materials Analysis Laboratory
Houston, Texas

July, 2014





Controlling Heat in Aerospace



Picture of Space Shuttle During Atmospheric Re-entry
taken from ISS





Analytical Chemistry Laboratory Equipment



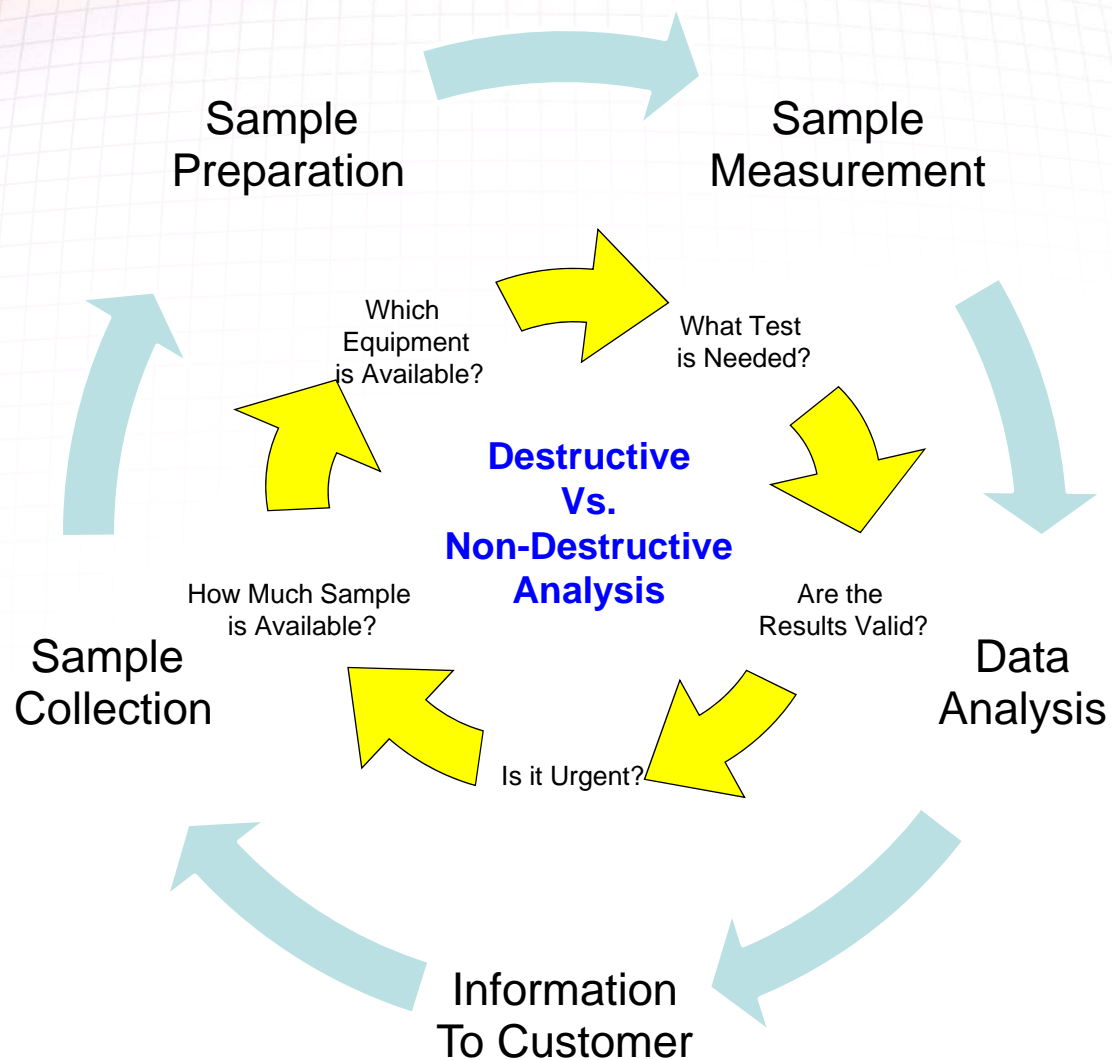
Key Laboratory Equipment

- Optical Instrumentation
 - UV-Vis, Fluorimeter, Solar Reflectance, Infrared Emittance, Raman
- Thermal Analysis Instrumentation
 - DSC, DMA, TGA, TMA, LFA, Rheometer
- Chemical Analysis Instrumentation
 - FT-IR, Ion trap GC-MS, Py-GC-MS, TGA-MS, TGA-IR





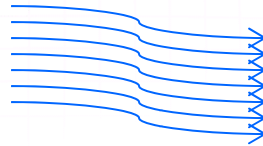
The Analytical Chemistry Cycle





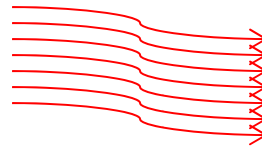
Optical Vs. Thermal Techniques

Light



Reflectance
Emittance
Absorbance/Transmission
Fluorescence
UV-Vis Absorbance
FT-IR Analysis
Raman Analysis

Heat

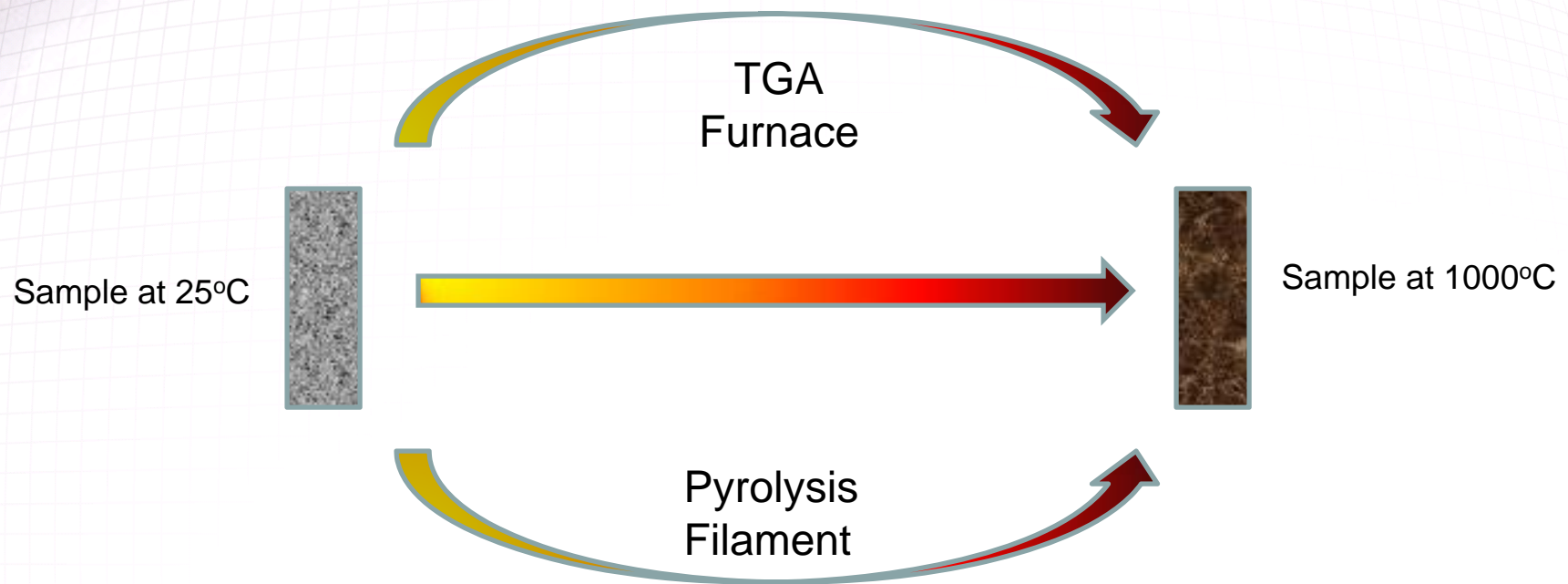


Material Curing
Thermal Transition-T_g
Melting Point/ Boiling Point
Residual Solvent
Identification of additives
Material Decomposition
Elimination of labile functional groups
Identification of Material Components
Identification of Inorganic Components



Controlling Heat Exposure

Thermal Analysis
Slow: minutes to hours

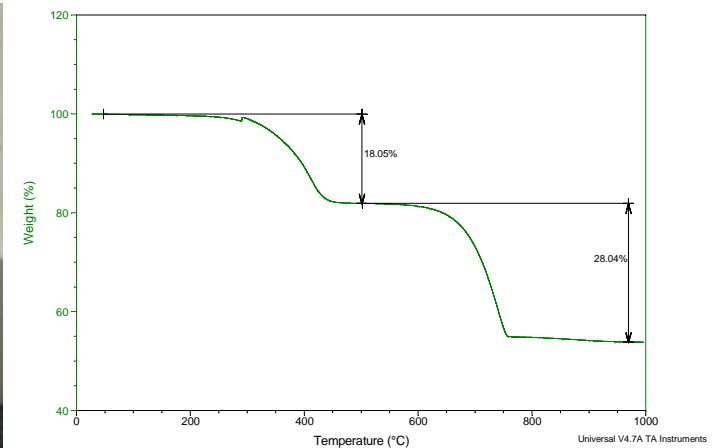


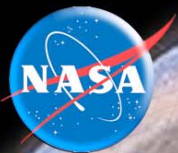
Fast: microseconds to seconds
Thermochemical Analysis



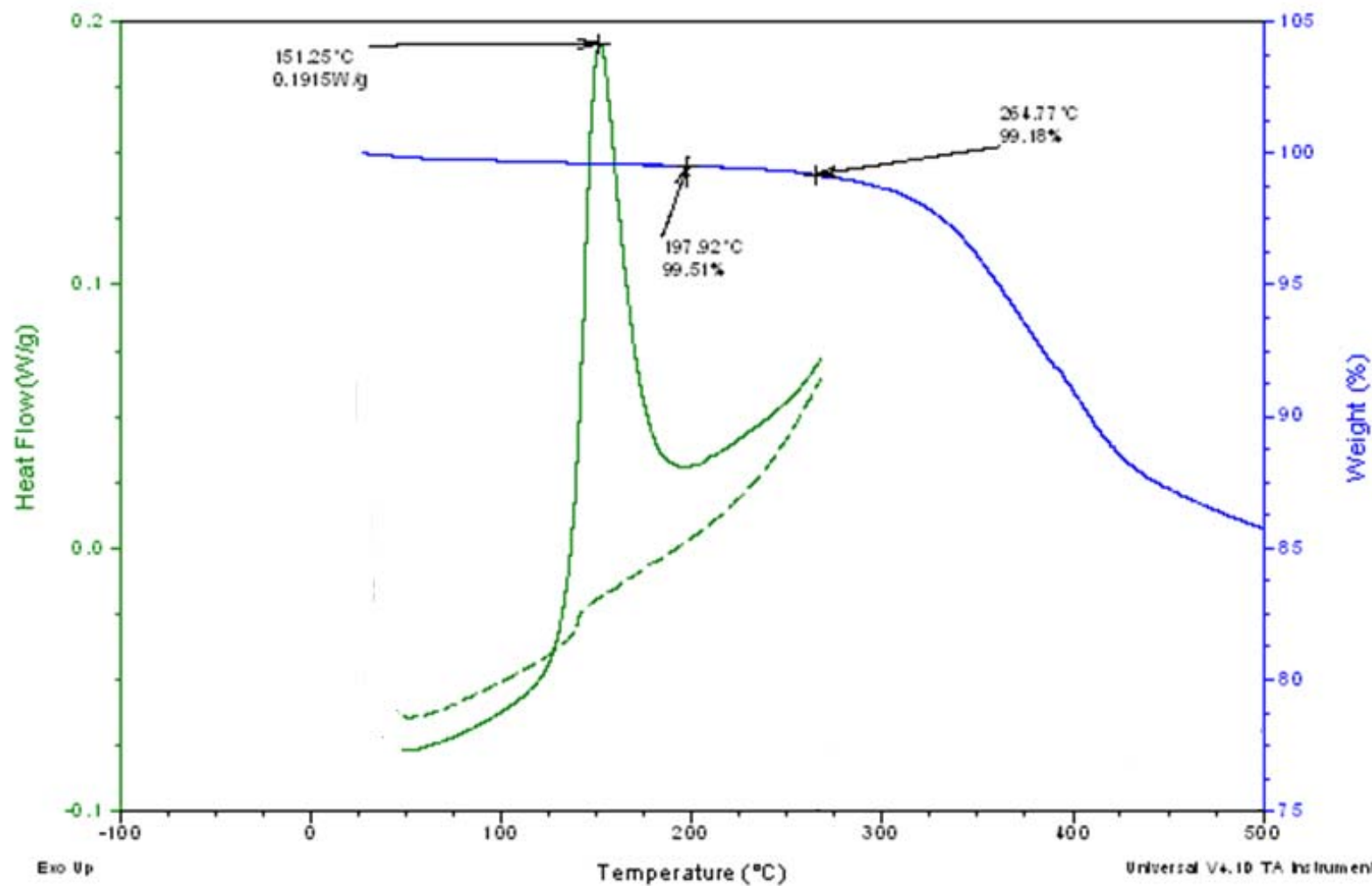
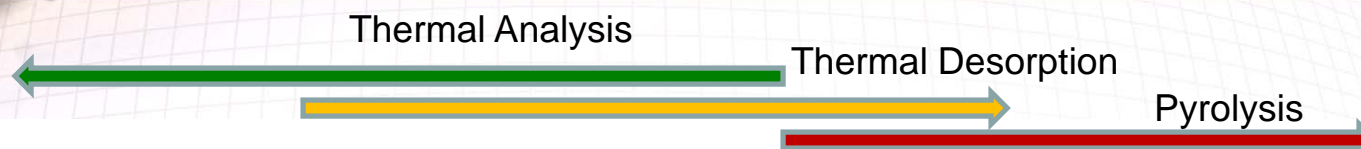
Thermogravimetric Analysis (TGA)

- A TGA instrument consists of an analytical balance and a furnace.
- A small sample of material is heated and its change in mass is measured as a function of temperature.
- Experiments can be conducted under inert or oxidizing atmospheres.
- Information gained from TGA includes:
 - Thermal stability for conducting additional thermal analysis
 - Identification of the number of components in the sample if the decomposition temperatures are different
 - Residual mass for assessing the extent of inorganic additives



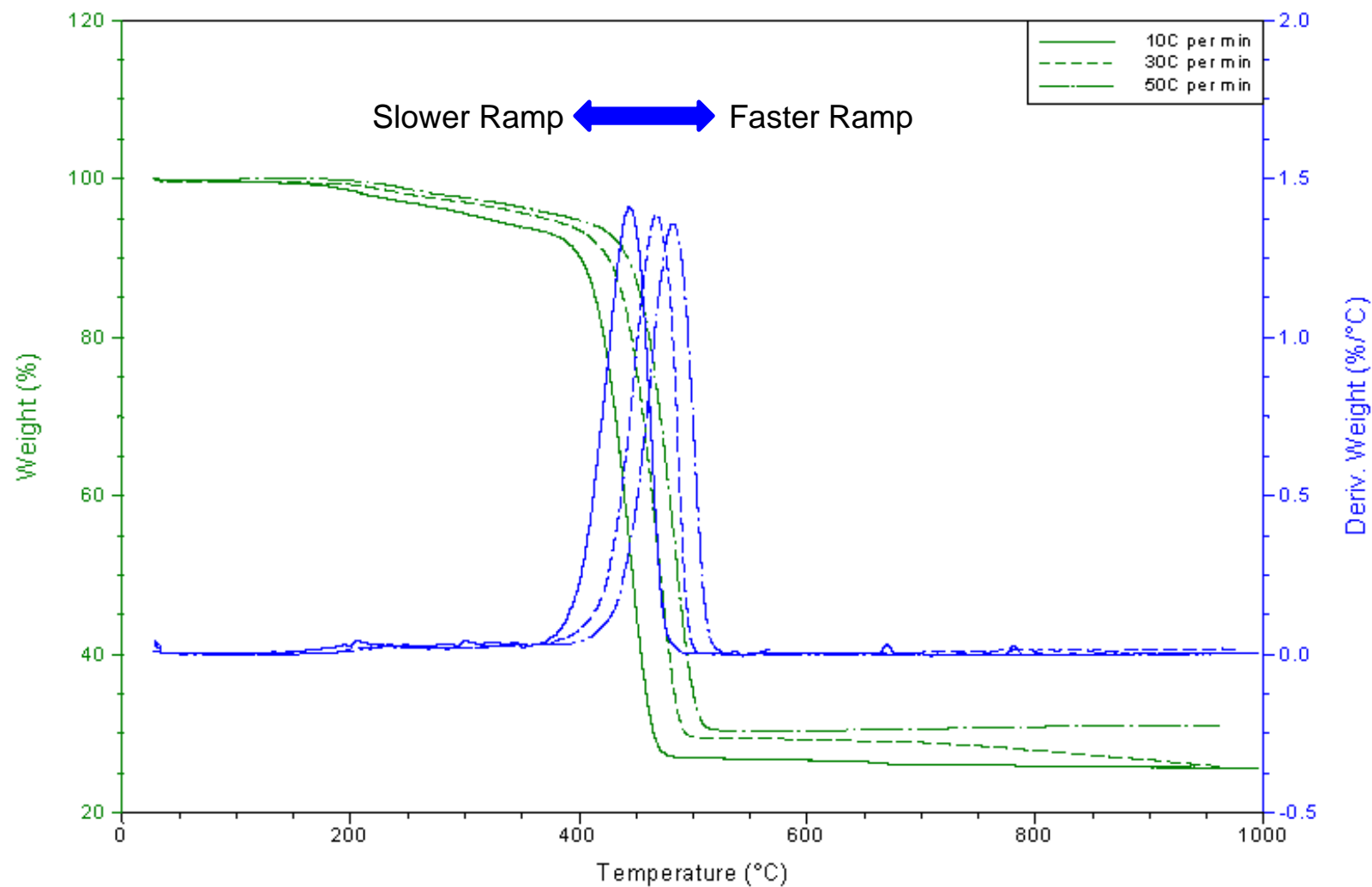


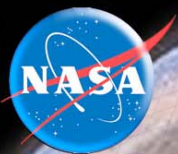
Thermal Analysis of Composite





The Influence of Temperature Ramp Rates





Pyrolysis for GC-MS of Solids

- Sample size is relatively small:

50 to 200 μg is sufficient for solids
50 to 200 nL is sufficient for liquids

- Sample preparation is easy:
Place sample inside 1.5 inch quartz tube containing filler tube and plug with glass wool.
- Samples can be solids, gels, viscous liquids, greases, crystalline, emulsions, foams, fabrics
- Pyrolysis temperatures are almost instantaneous
- Sample components can be quantified with the use of software



Pyrolysis is the thermal degradation of any substance through the fast application of heat.



Pyrolyzers: Filament Versus Furnace

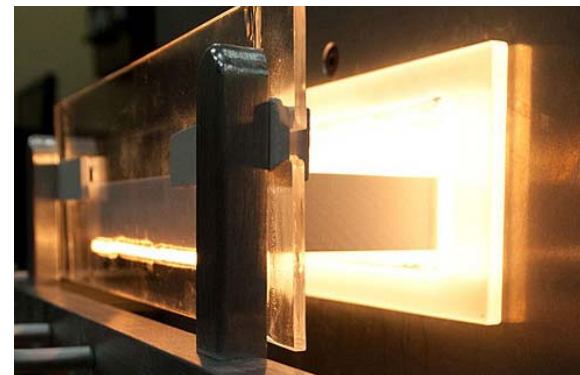
CDS Platinum Filament

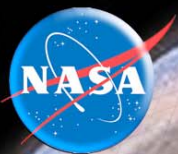
- Heating Rate: $\sim 20,000^{\circ}\text{C}$ per sec
- Max Temperature: 1400°C
- Cooling Rate: $> 1000^{\circ}\text{C}$ per sec
- Fast Heating, Fast Cooling



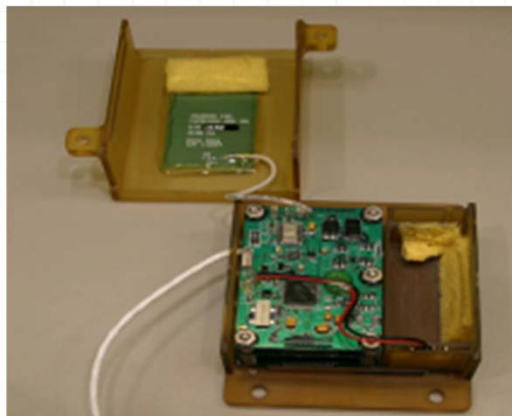
Microfurnace

- Heating Rate: $\sim 50^{\circ}\text{C}$ per min
- Max Temperature: 800°C
- Cooling Rate: 25°C per min
- Slow to Heat, Slow to Cool



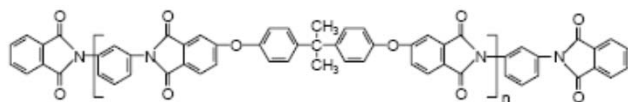
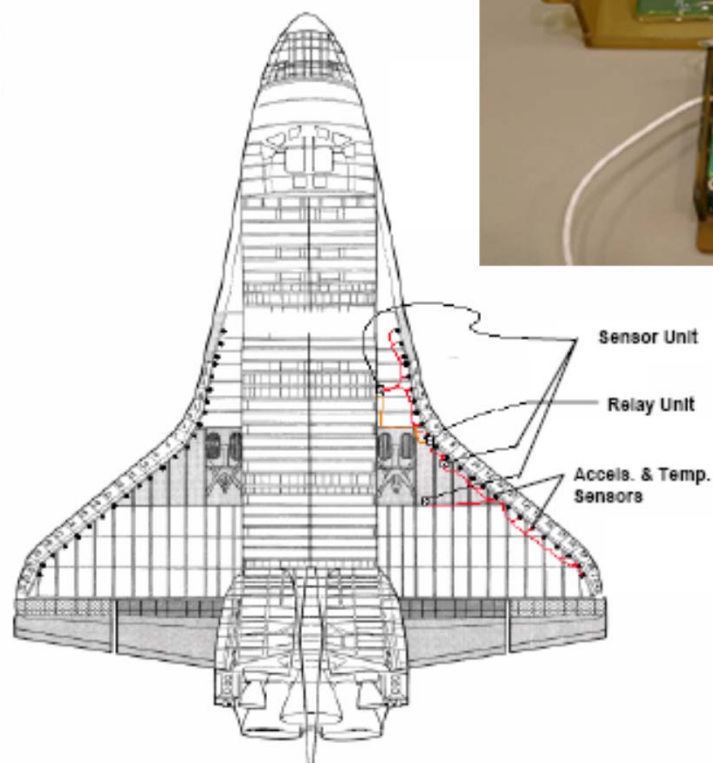


Flash Pyrolysis-GC-MS of Ultem 1000

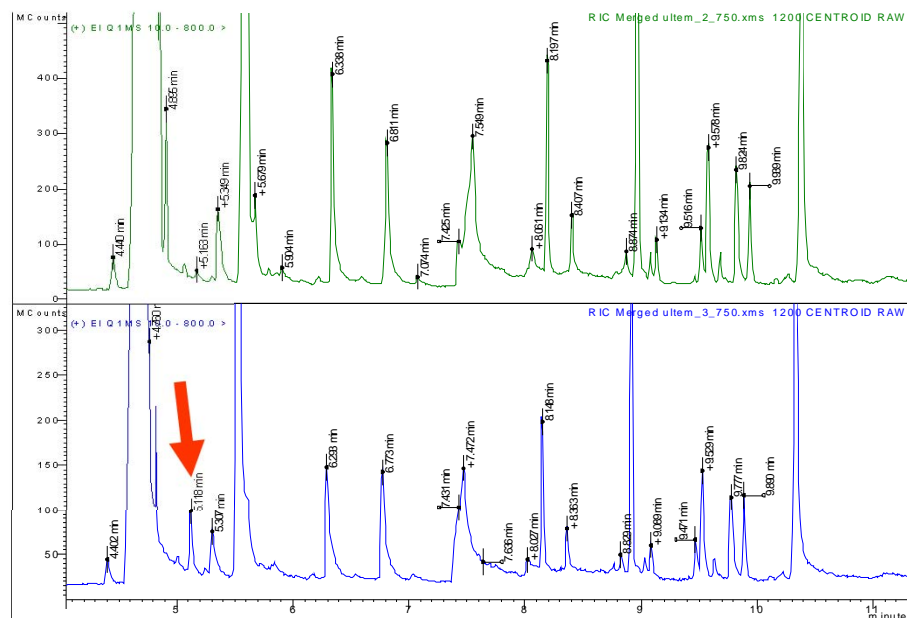


Relay sensor boxes along the shuttle's wing leading edge were composed of Ultem 1000. One lot used to make these relay sensor boxes had failed

Various manufacture lots of sensor boxes were analyzed by Py-GC-MS and an extra peak was noted in one of those lots. The extra peak was due to dichlorobenzene, a solvent used during manufacture of Ultem 1000.

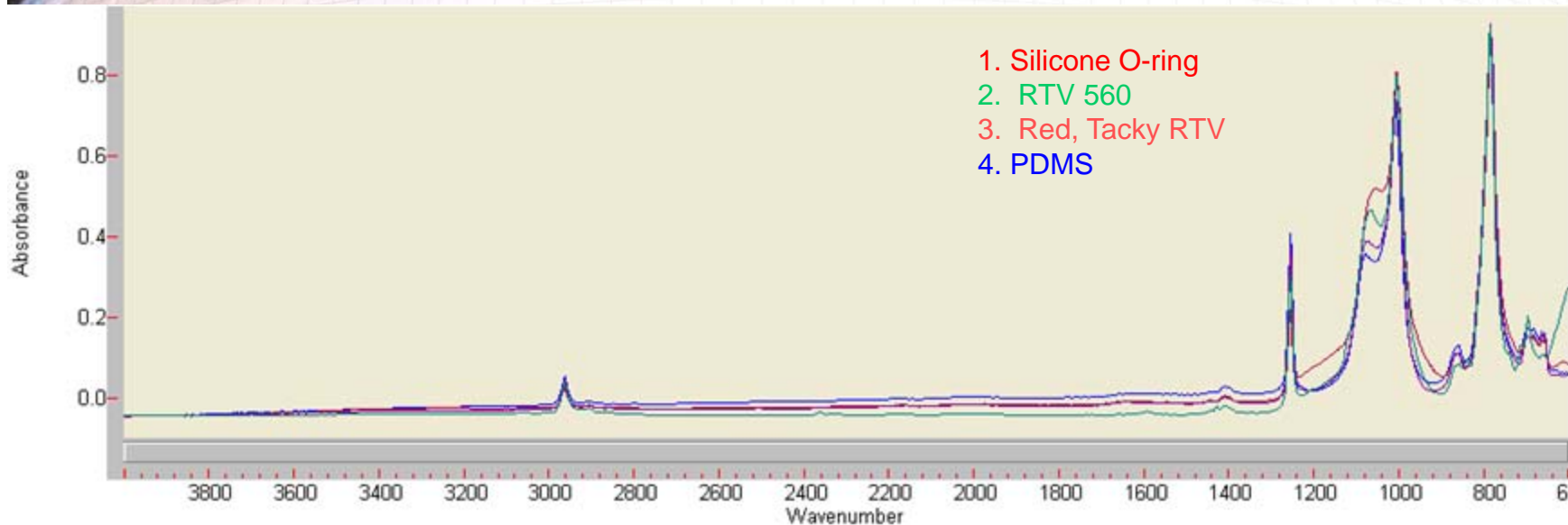


Ultem 1000®

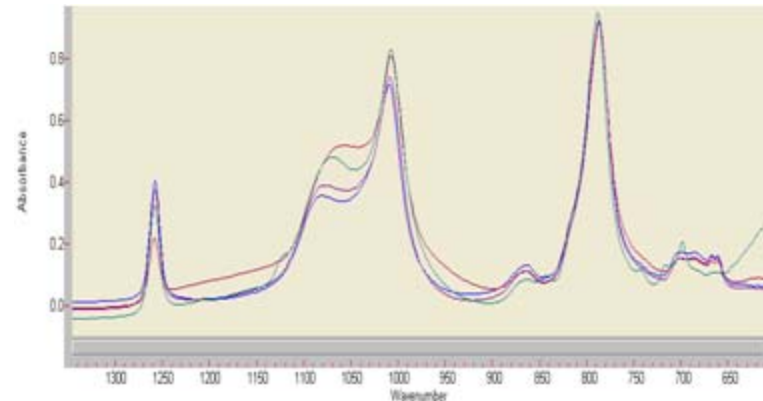




FT-IR Analysis of Silicone Materials

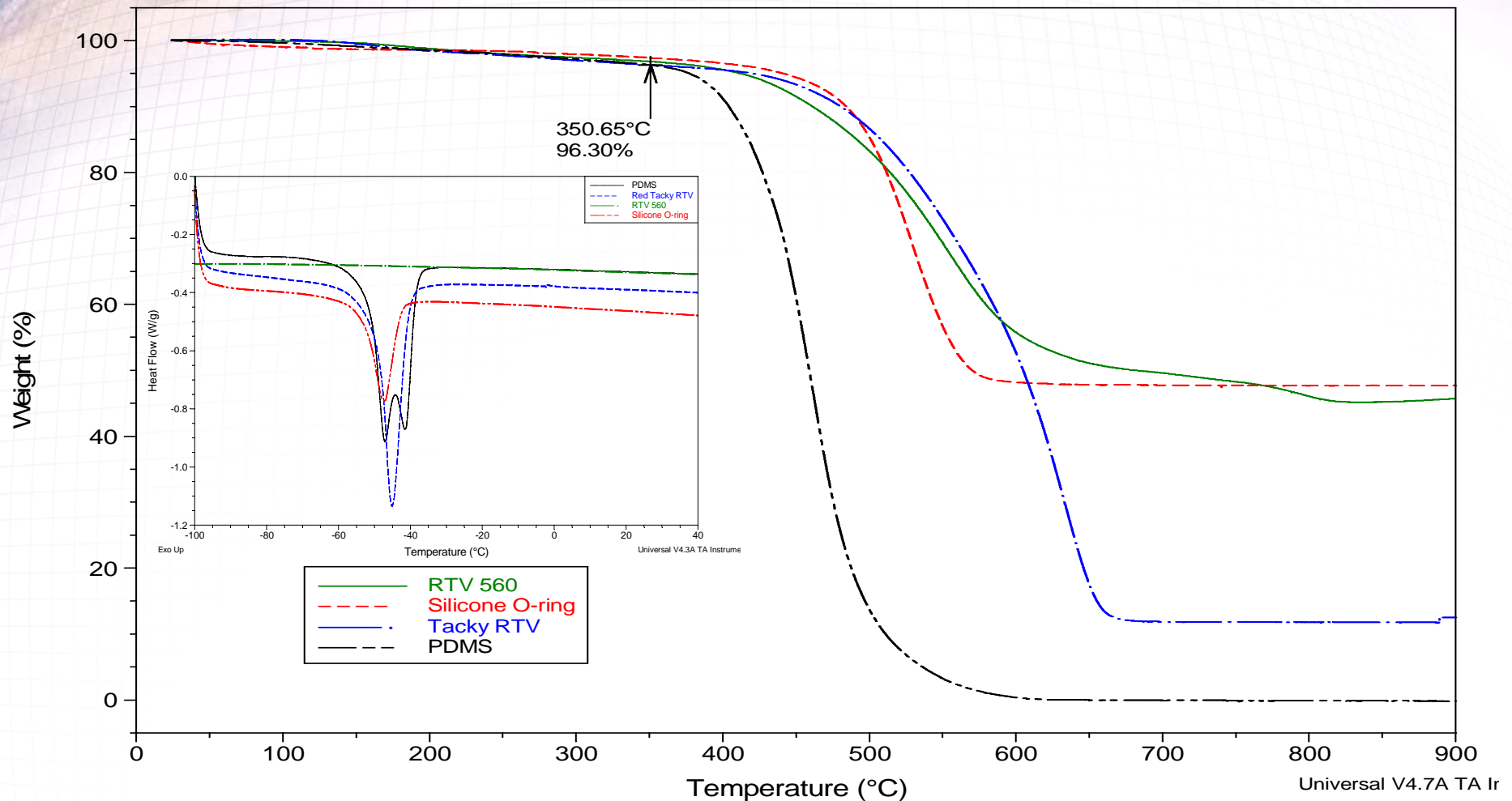


FT-IR is a non-destructive technique that is very diagnostic. However, if infrared light cannot penetrate the sample, any signal obtained through reflectance is only valid for the external surface of a sample.





Thermal Analysis of Silicone Materials

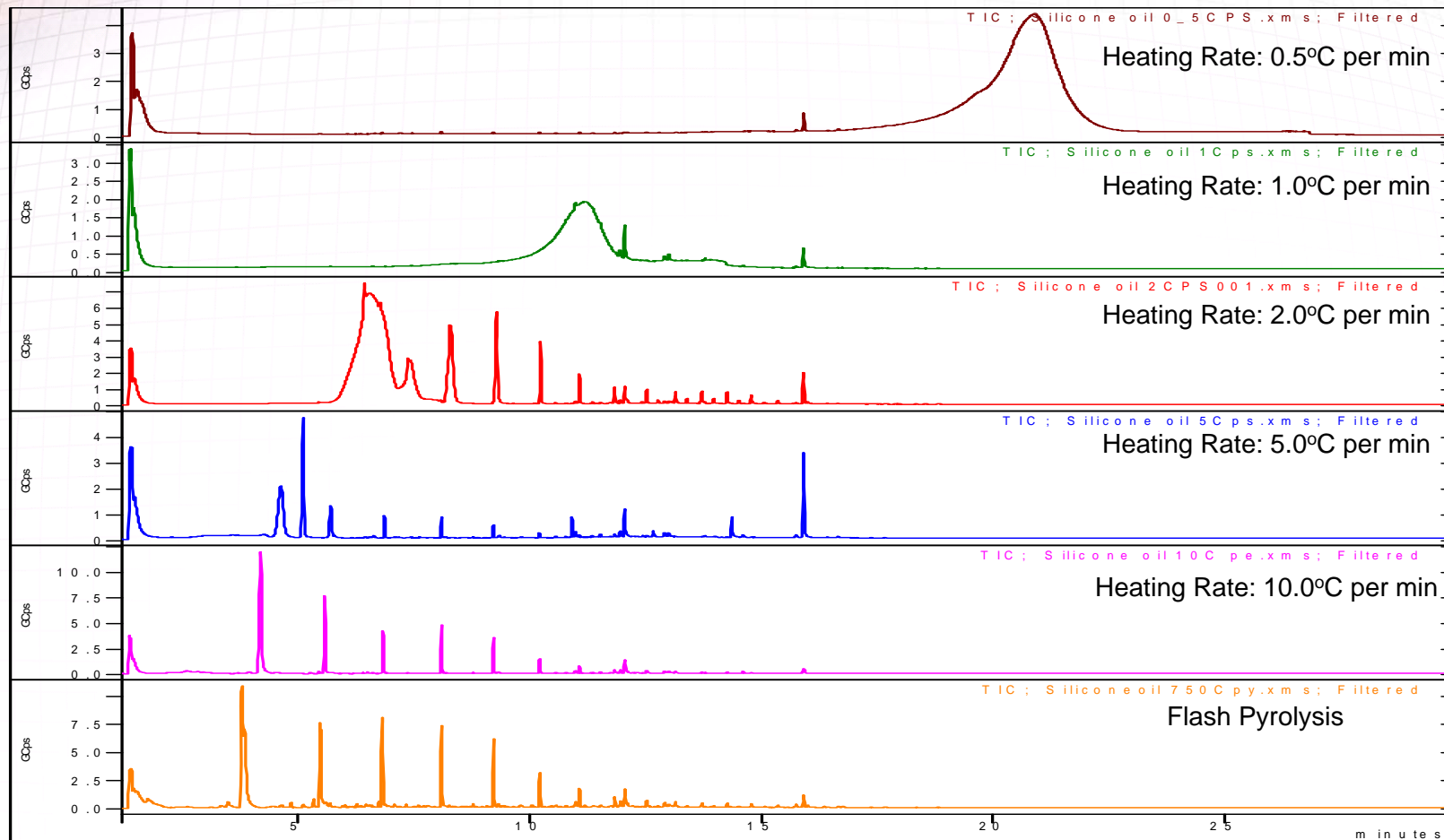


The Silicone samples that were nearly identical by FT-IR displayed very different properties by thermal analysis.



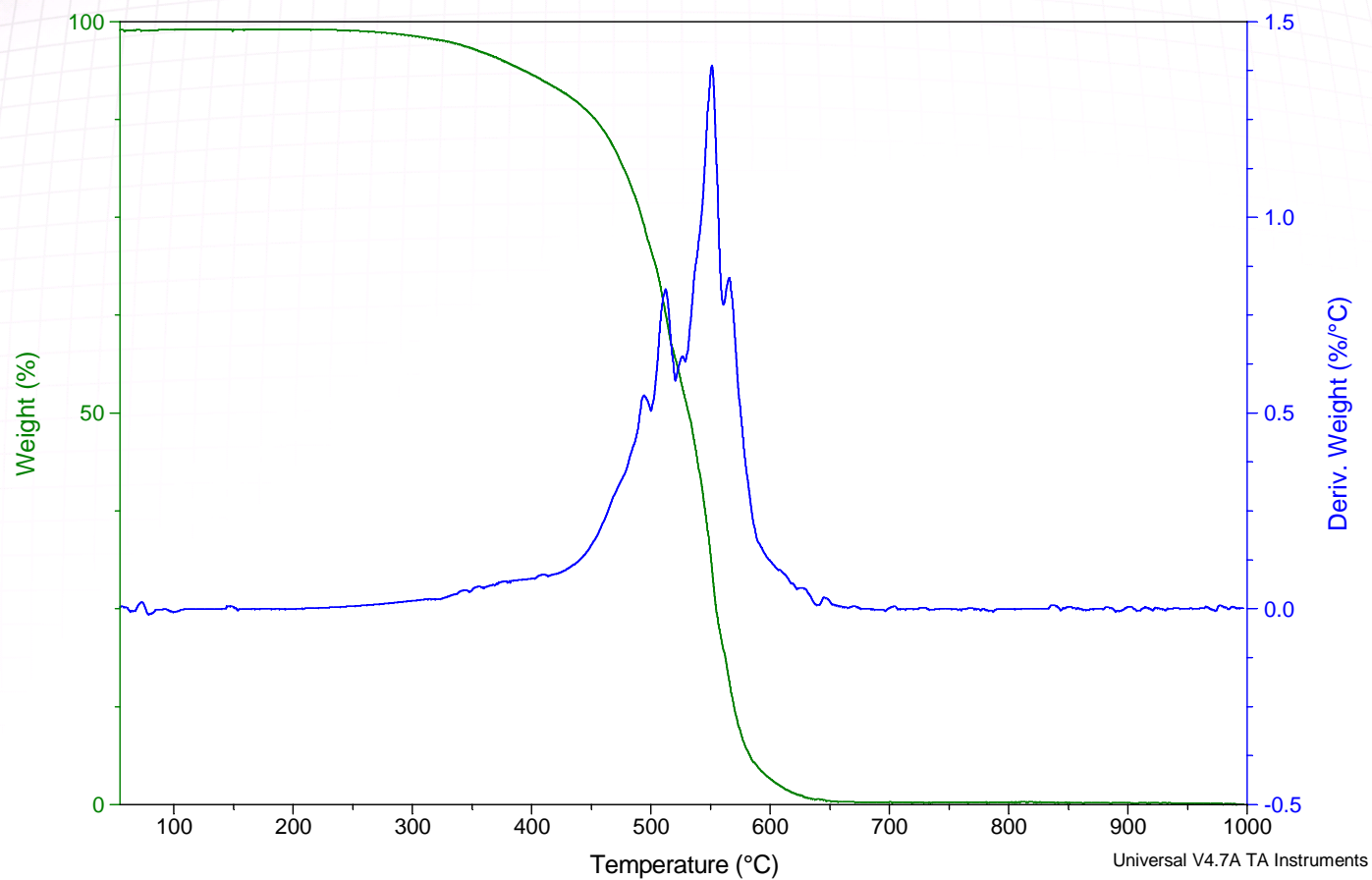
Pyrolysis of Silicone Oil at Different Temperatures

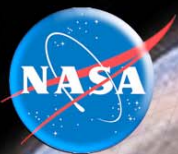
Chromatogram Plots



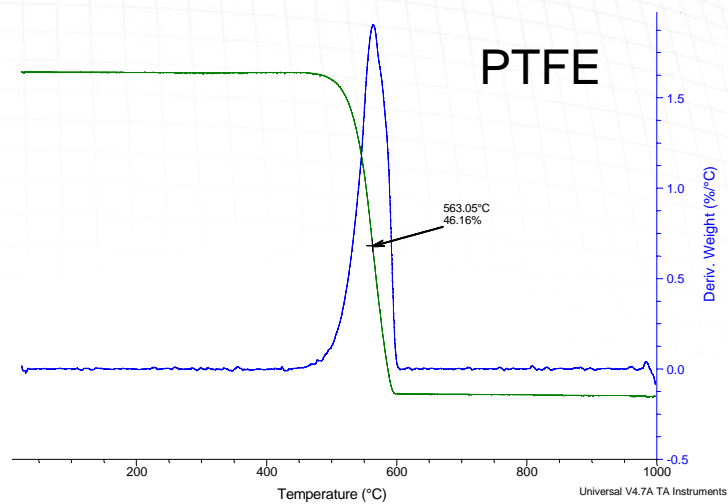
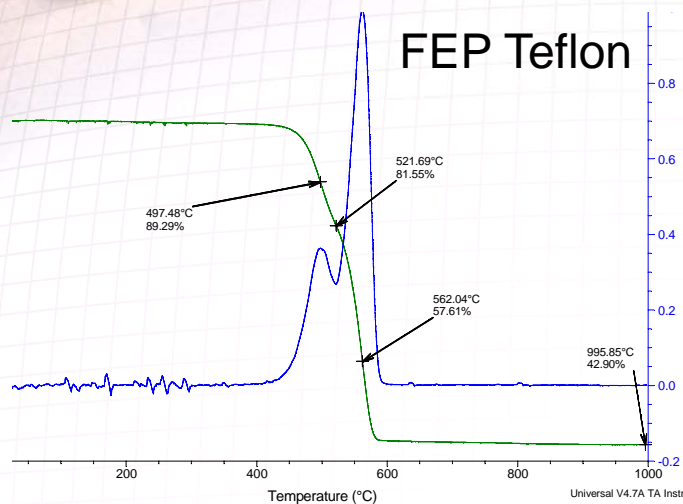


TGA Analysis of Silicone Oil

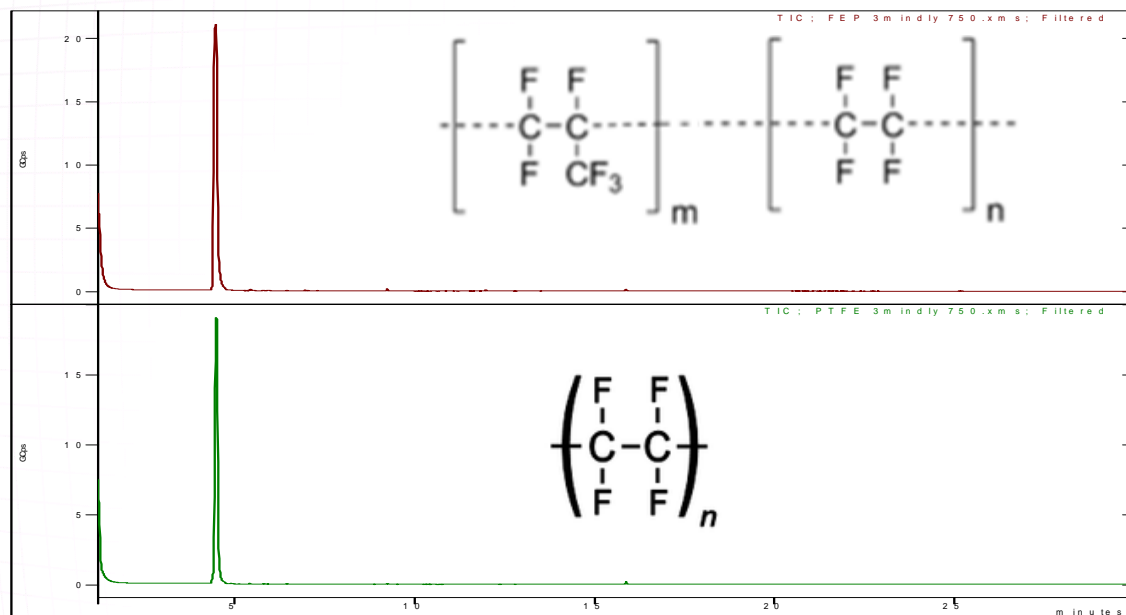




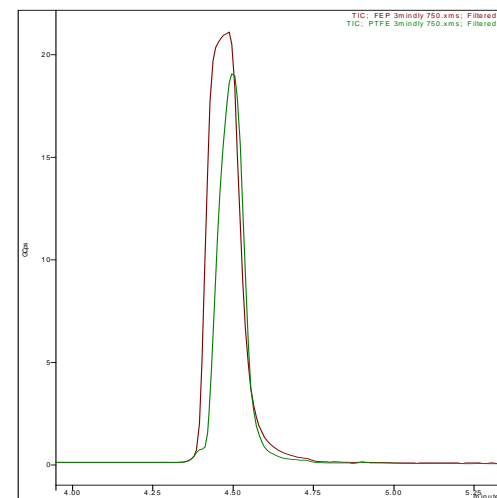
FEP Vs. PTFE Teflon



Chromatogram Plots



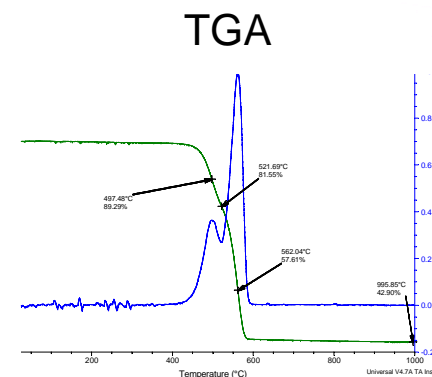
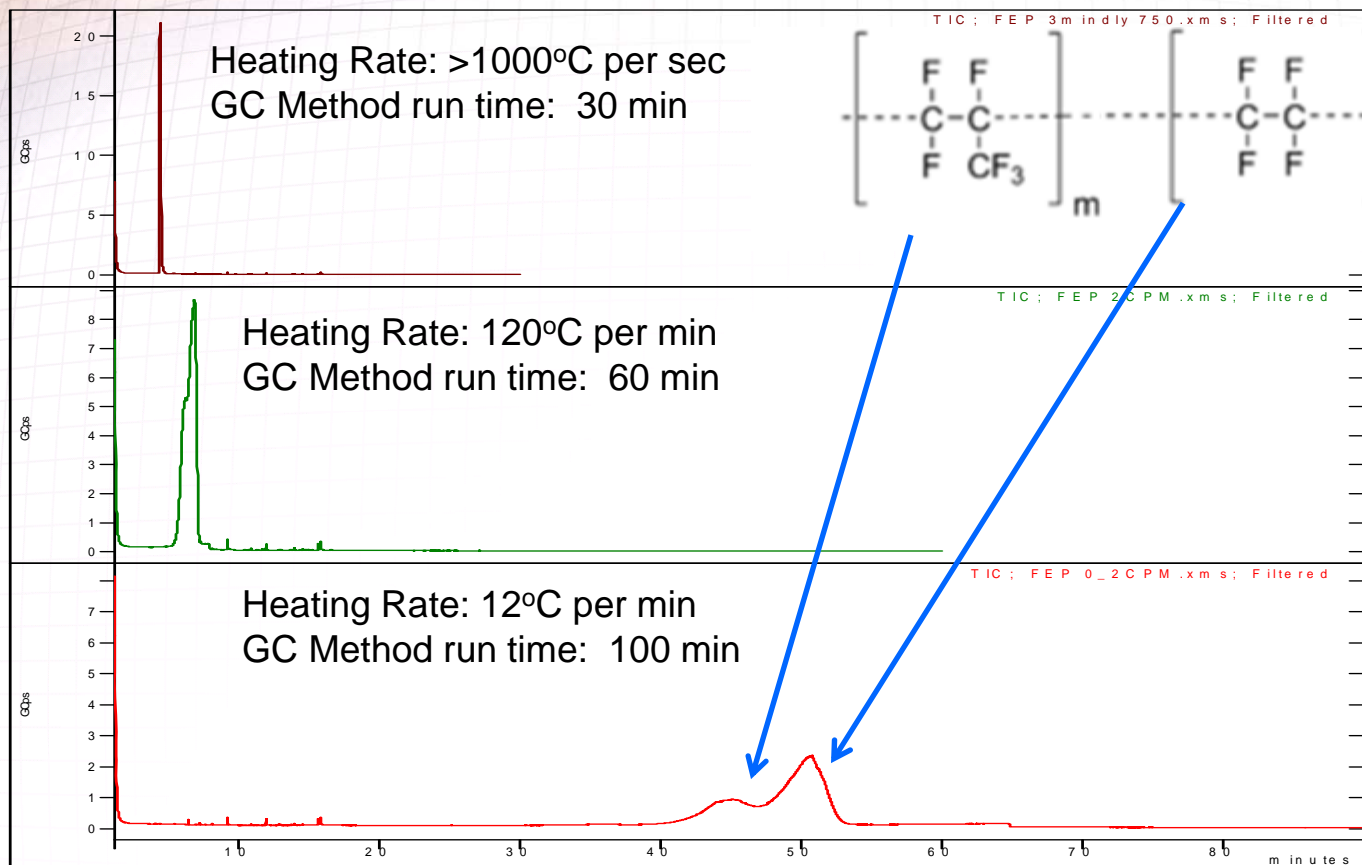
Overlaid Chromatogram Plots





FEP Teflon Heated at Different Rates

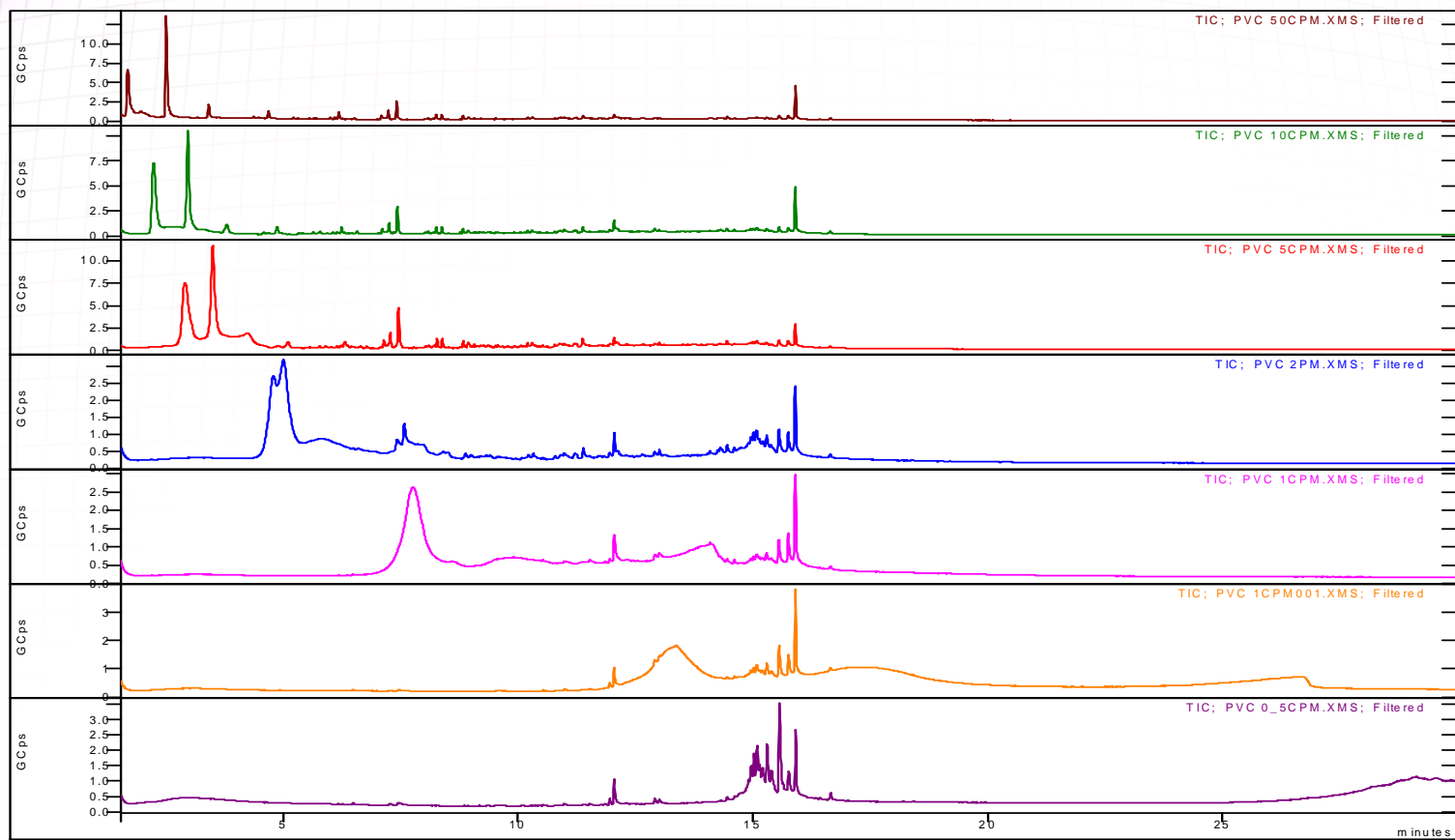
Chromatogram Plots



During pyrolysis, materials undergo thermal degradation via chemical pathways dictated by the thermal stability of the components. When pyrolysis is slowed to simulate TGA conditions, a thermal response pattern similar to what was observed with TGA first derivative plot is observed.

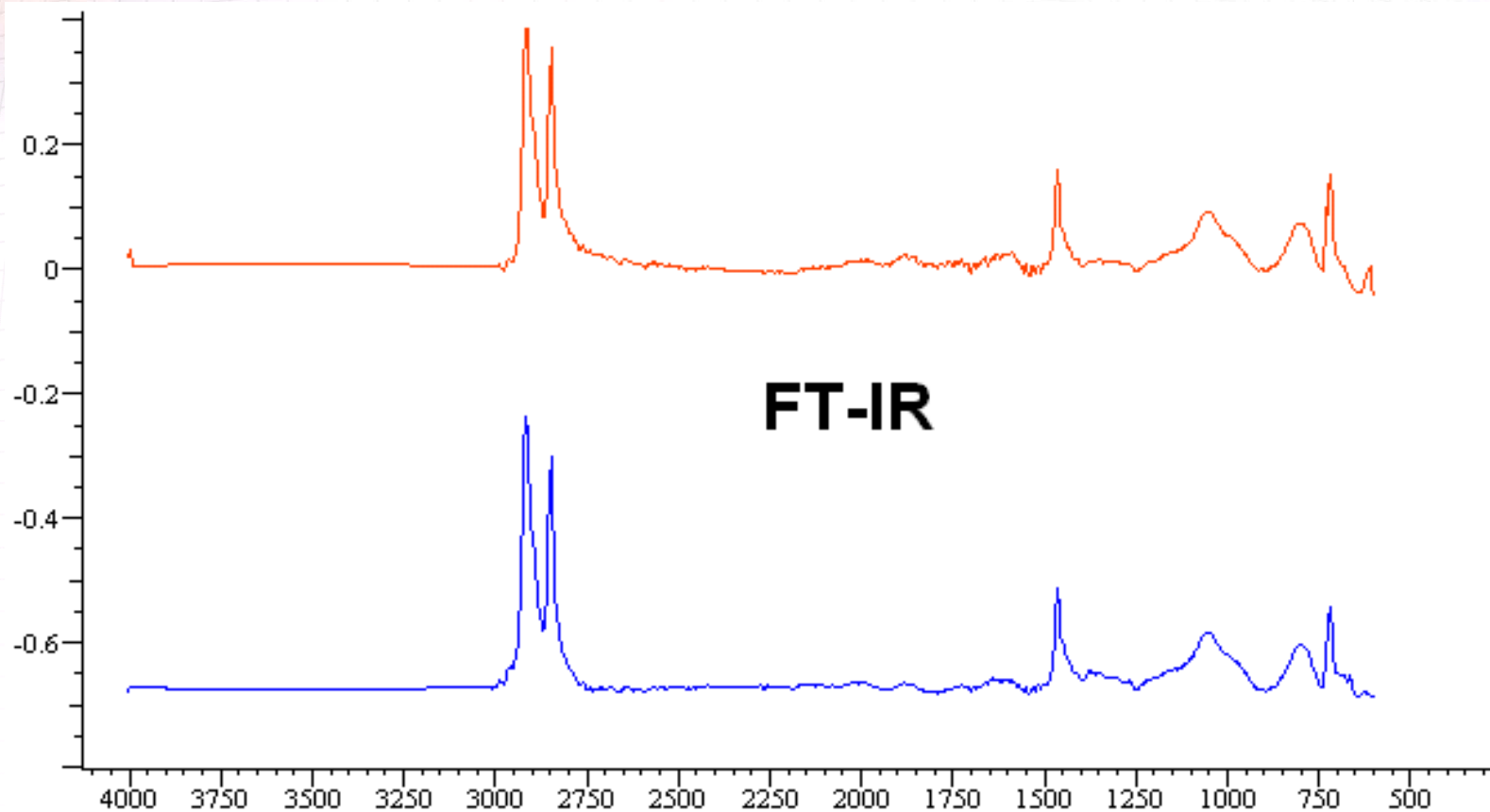


Chromatogram Plots





Spectral Analysis of HDPE and LDPE

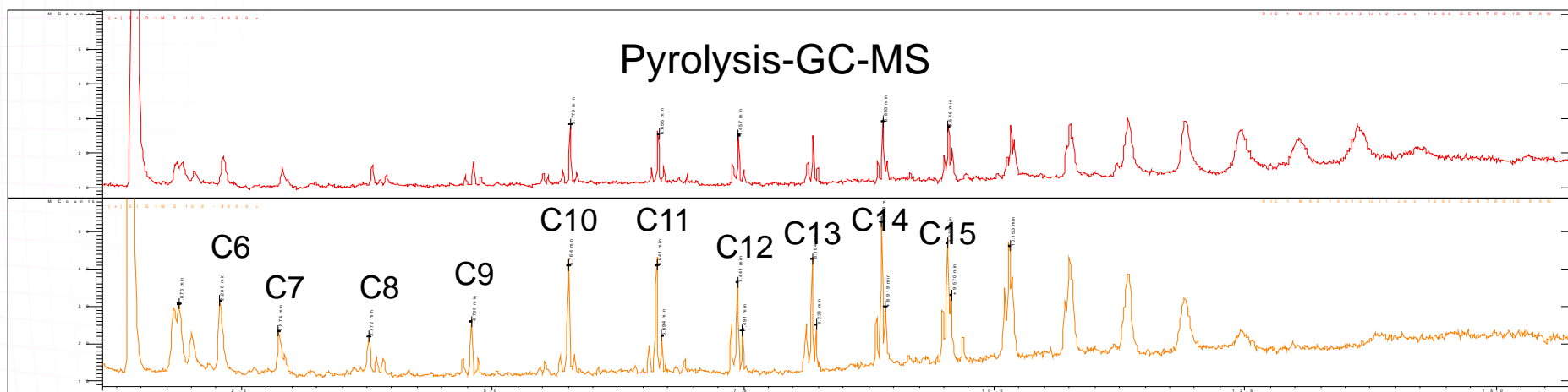
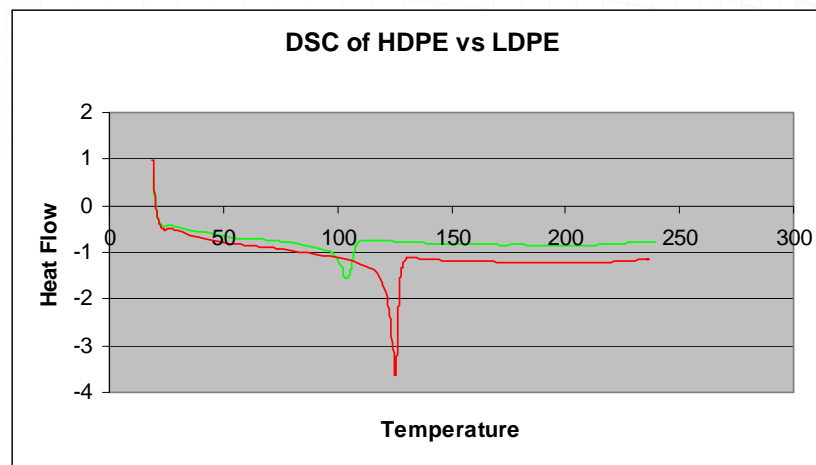
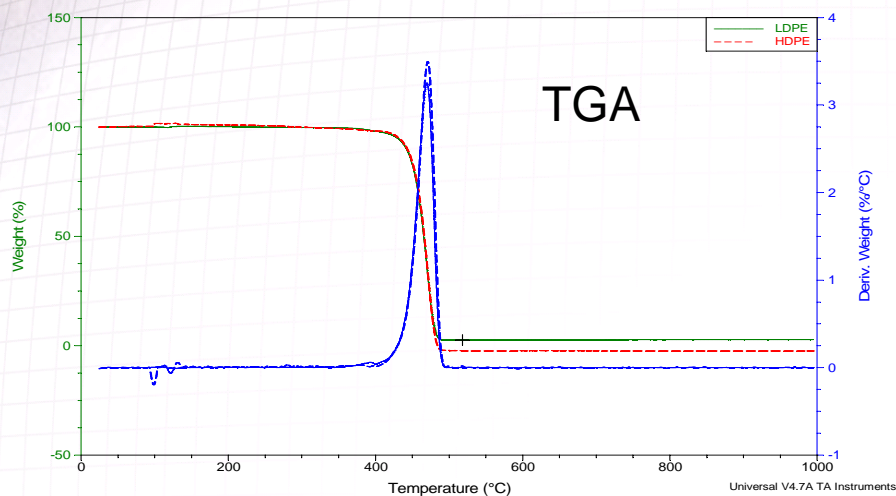


Many industrial laboratories have only one technique available for characterization of the manufactured product. In many situations, one type of analytical technique is not adequate for assessing the product.



Thermal Analysis of HDPE and LDPE

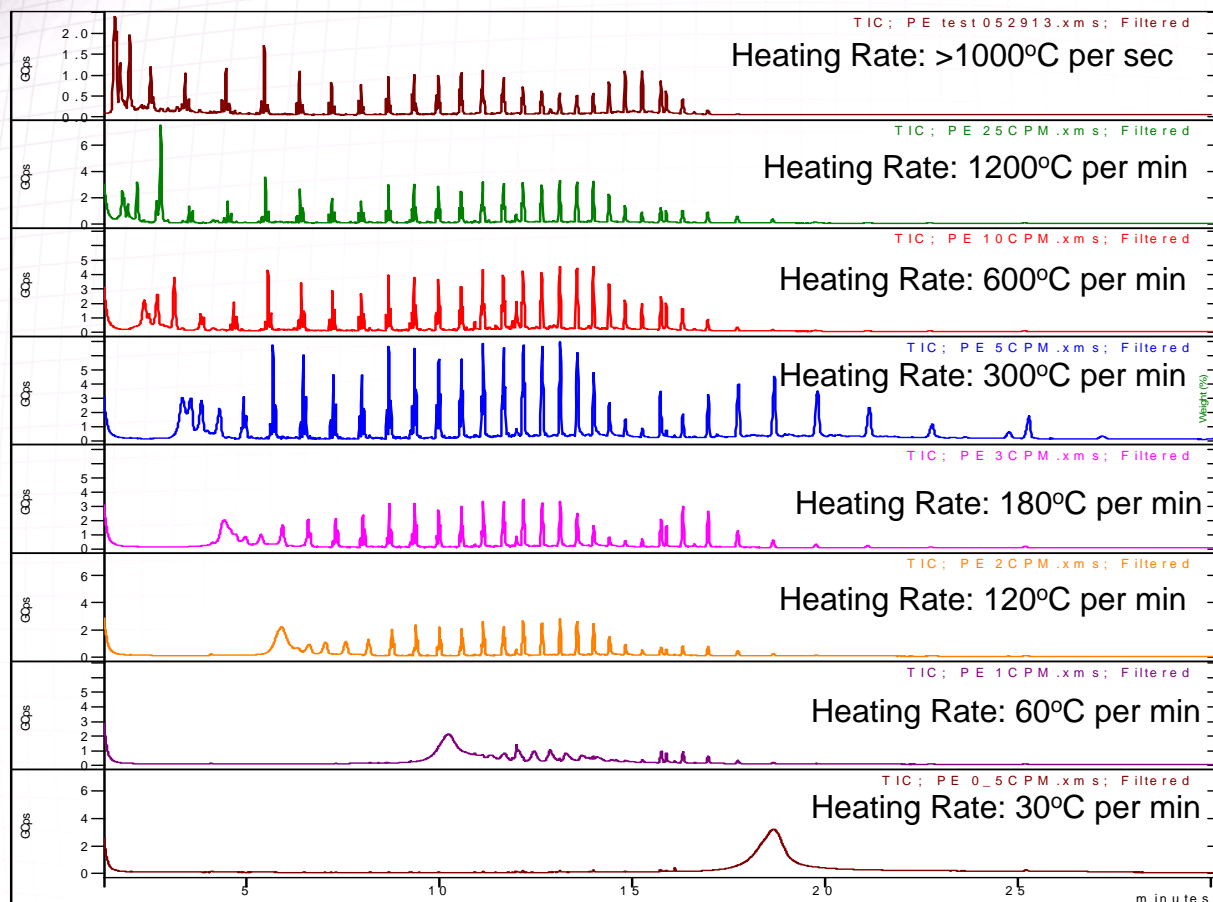
Polyethylene: $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$



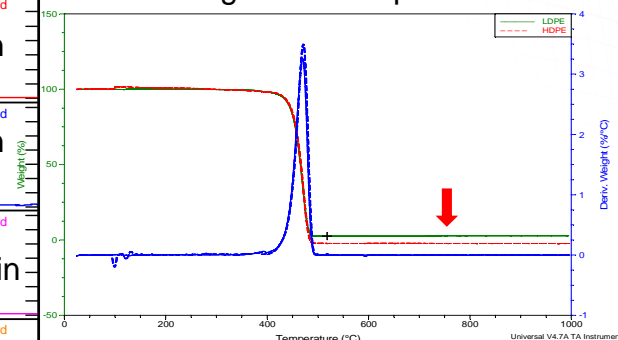


Temperature Ramp Pyrolysis

Heating PE in Pyrolysis chamber from 25°C to 750°C at different rates



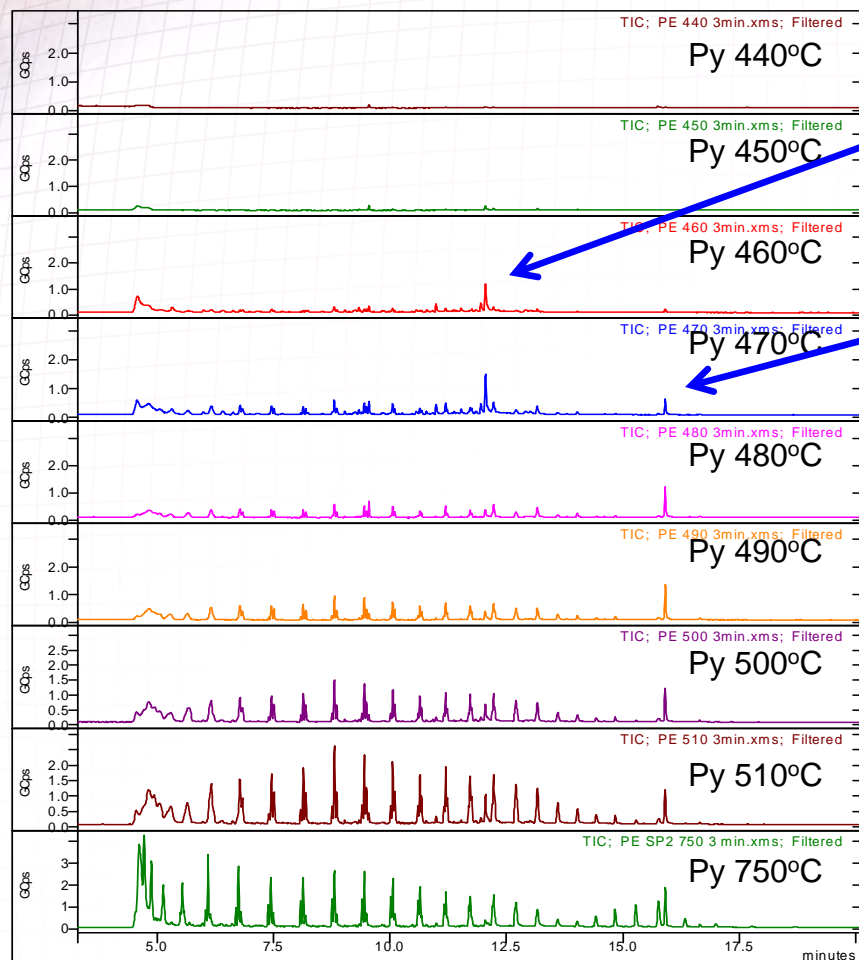
TGA
Heating Rate: 5°C per min



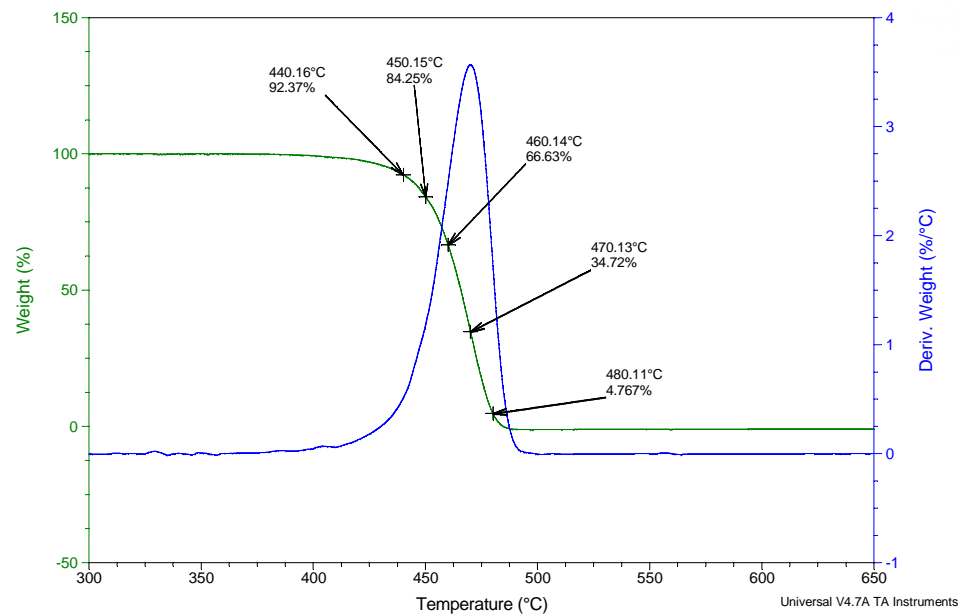
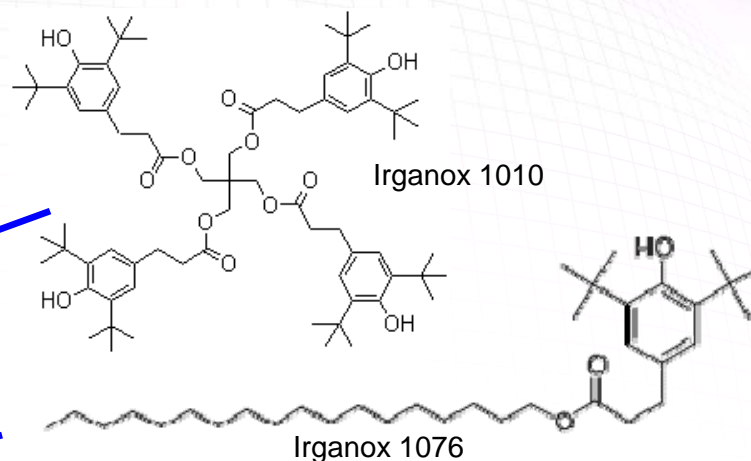


Correlating TGA and Pyrolysis Techniques

Chromatogram Plots



Pyrolysis at specified temperatures for 20 seconds

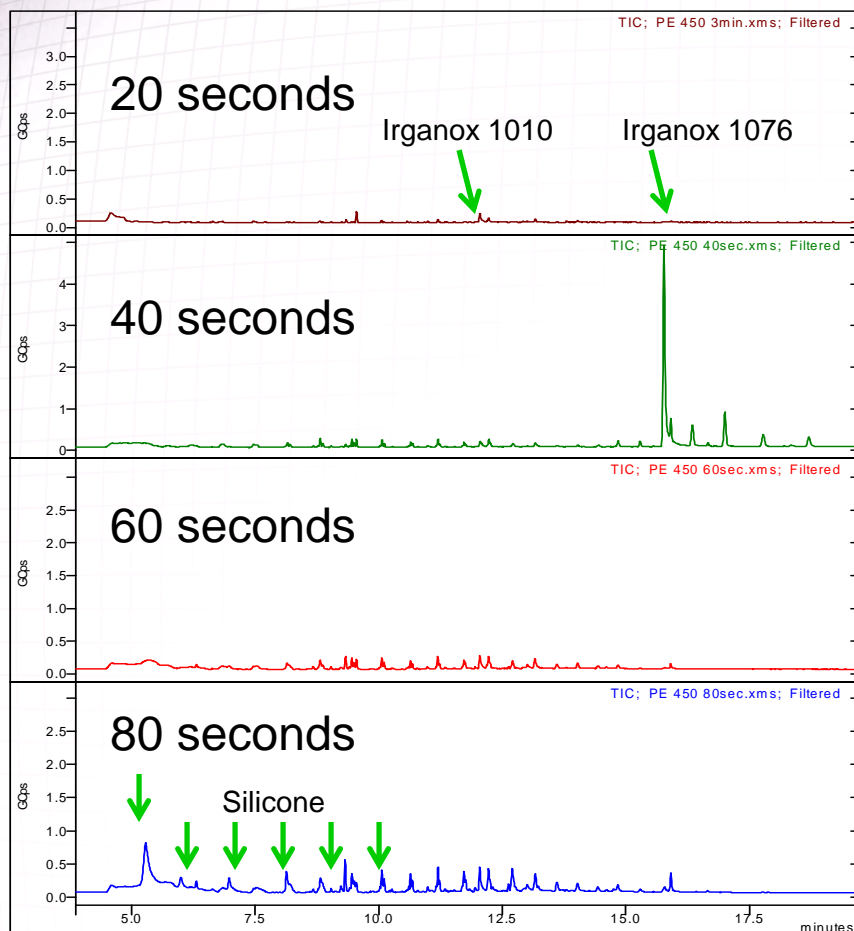




Thermal Analysis of PE

Pyrolysis at 450°C For Specified Duration

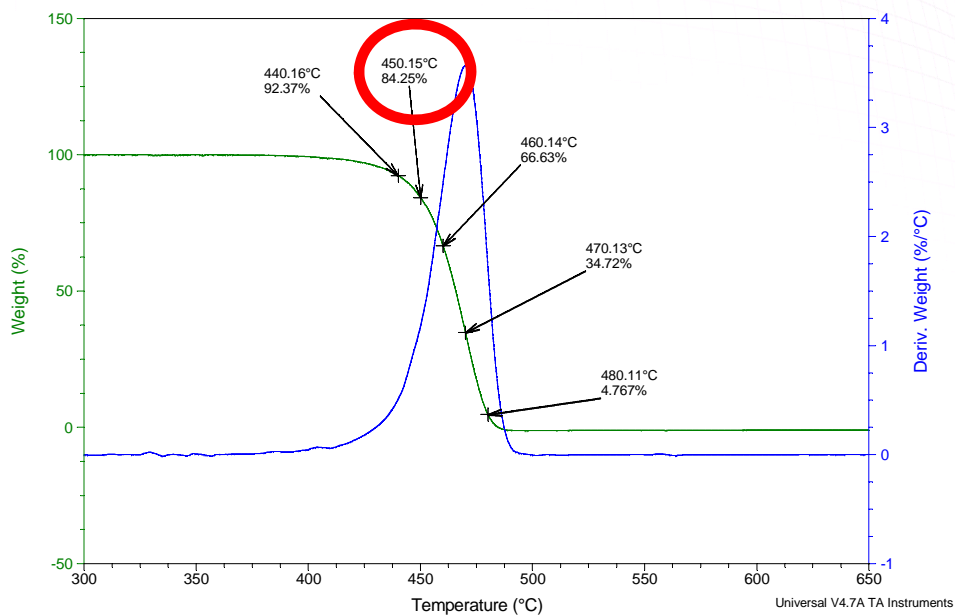
Chromatogram Plots



Sample: PE 5C per min
Size: 2.8770 mg

DSC-TGA

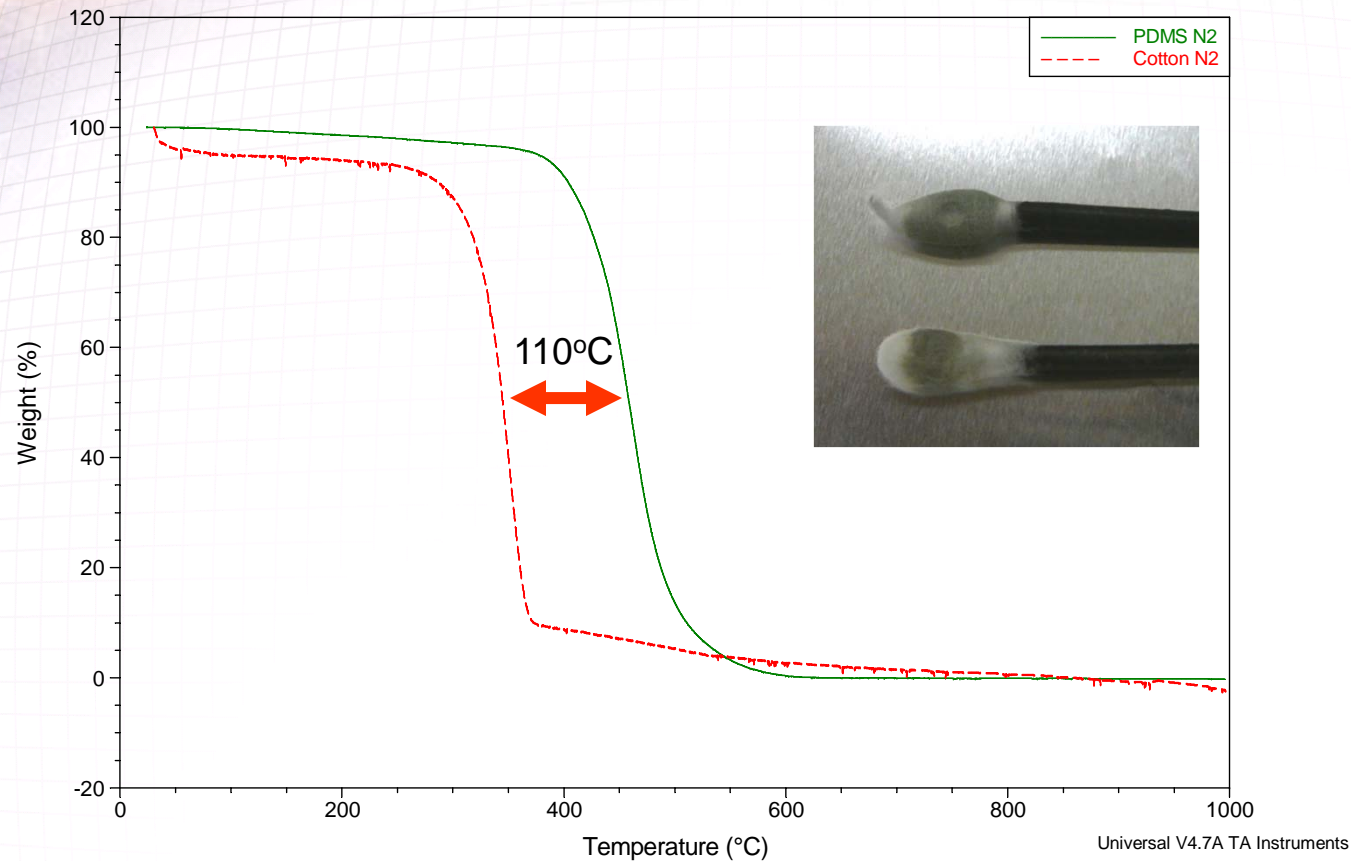
File: D:\Desktop\PE 5 Cpermin Nitrogen.001
Operator: RDevivar
Run Date: 24-Oct-2013 15:41
Instrument: SDT Q600 V20.9 Build 20



Modification of the thermal parameters at the onset of TGA degradation for PE can provide valuable information about the additives or contaminants.



Cotton Vs. Silicone

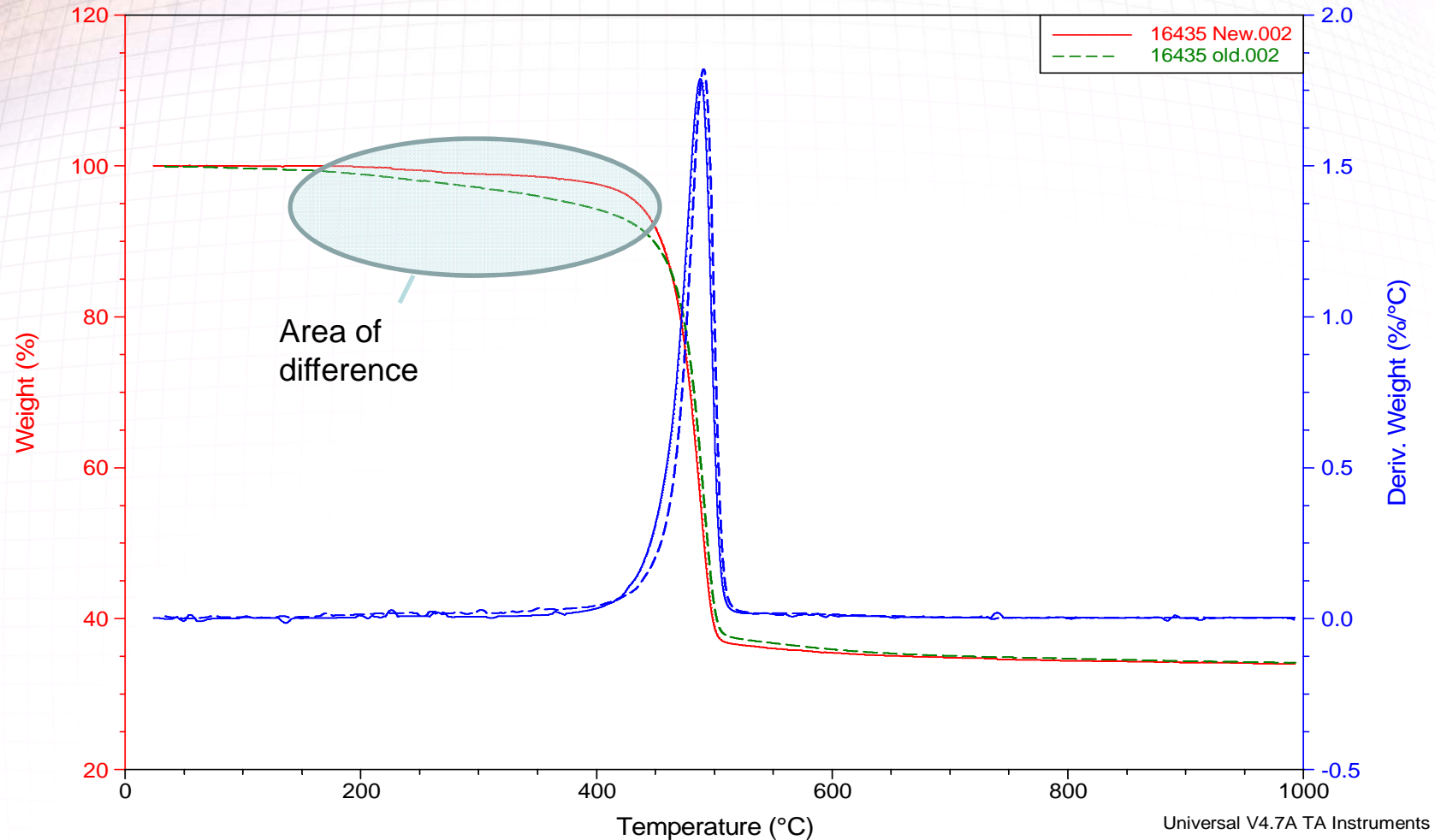


The large difference in thermal stability between cotton and silicones can be used to easily characterize the silicone sample collected on a cotton swab.

The cotton may be completely decomposed by application of heat without adversely affecting the silicone.



TGA Comparison of Gaskets

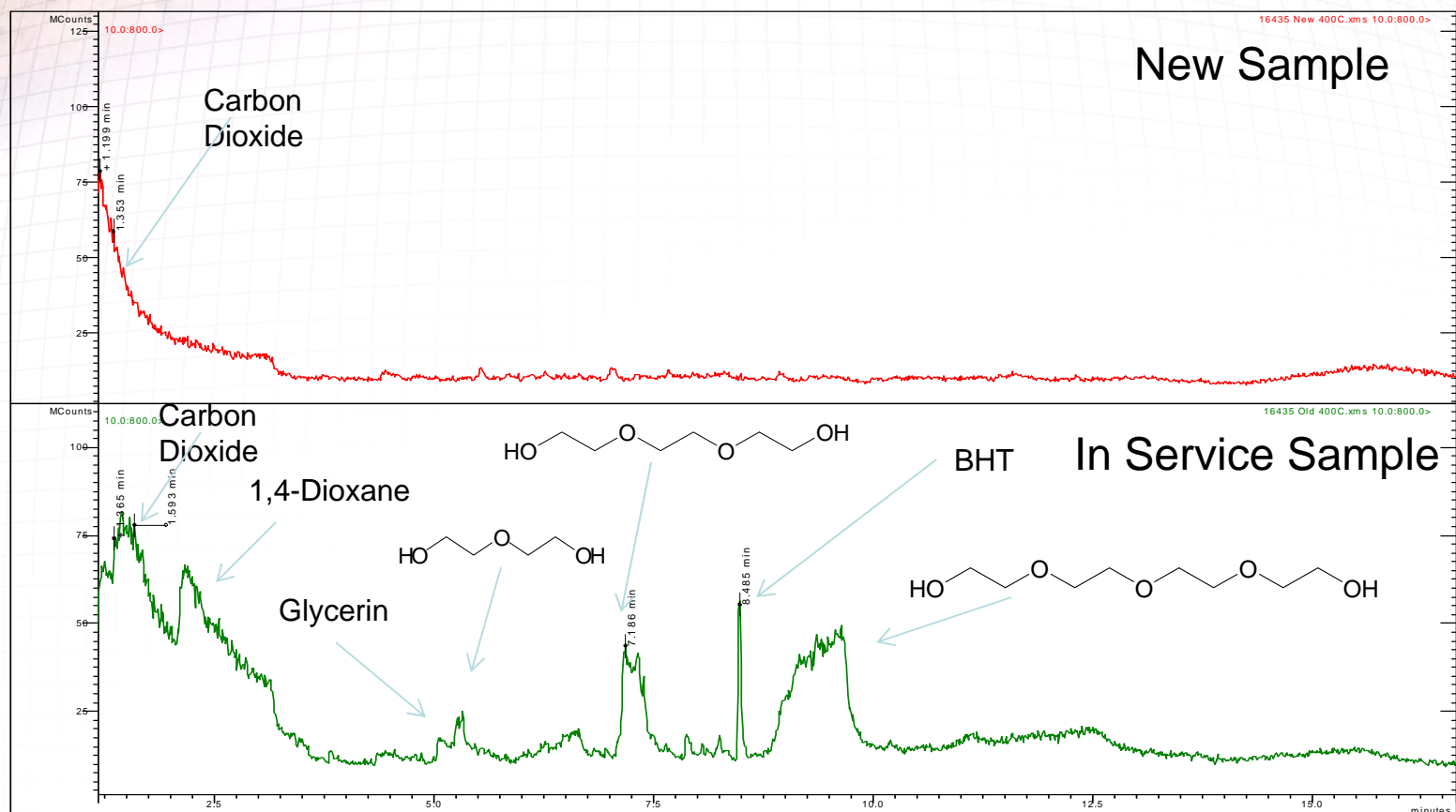


Under conditions of increasing temperature, the only difference between the two Viton Gaskets was found below 400°C, where the old sample lost a larger percentage of its mass compared to the new sample.



Thermal Extraction of Samples

Chromatogram Plots

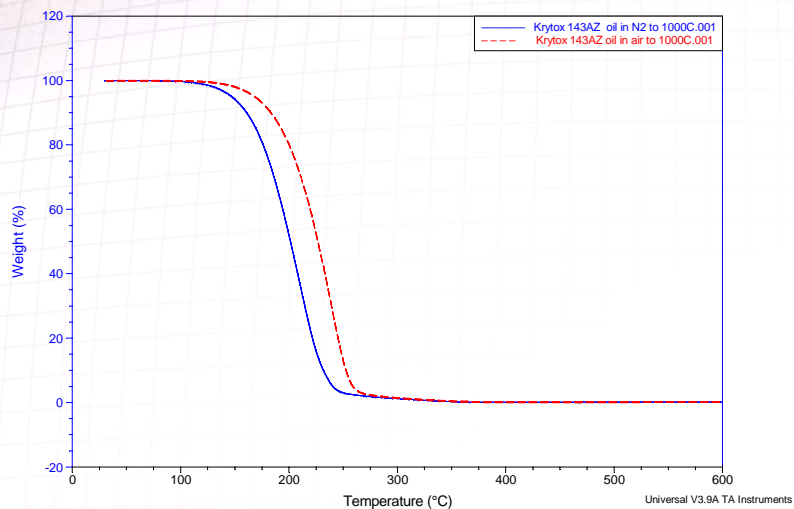


Thermal extraction of the two samples was performed to account for the difference observed in the TGA experiments at temperatures below 400°C. Such an experiment indicated the Old sample contained various fragments that are attributed to polyethylene oxide. Other substances found included Glycerin and Butylated hydroxy toluene (BHT).

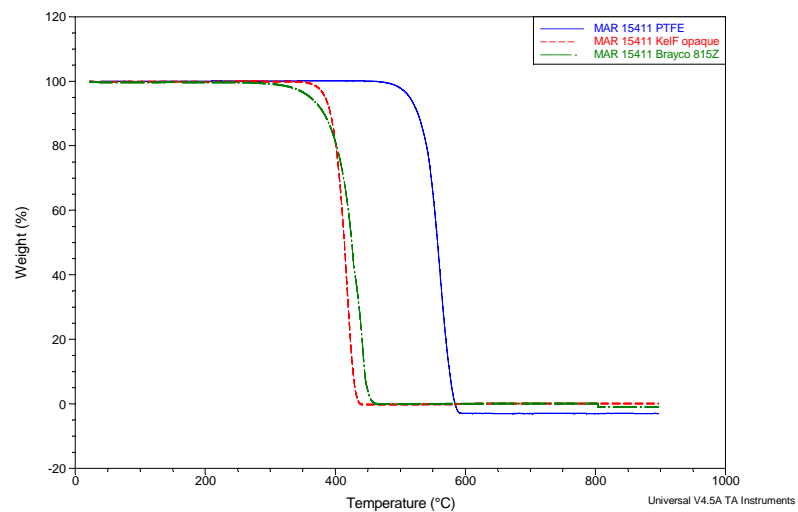
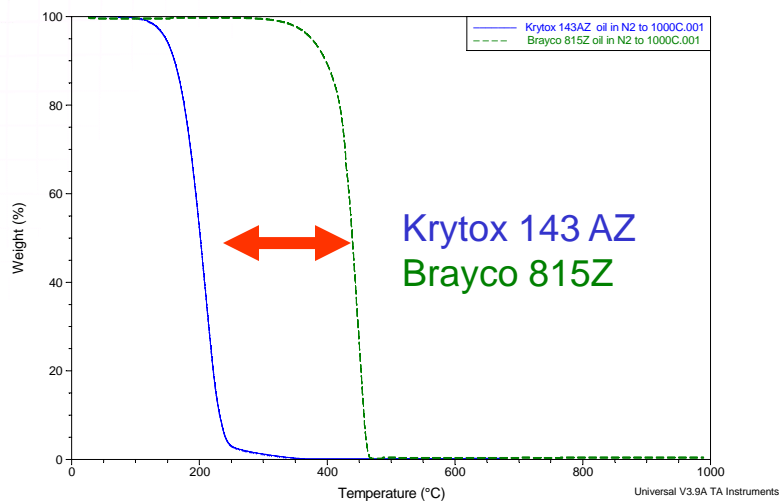
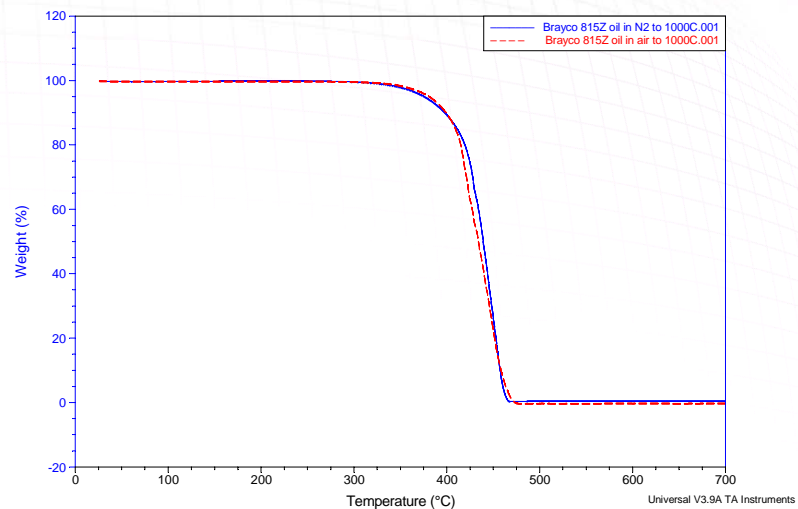


TGA Analysis of Fluorinated Materials

Krytox 143 AZ

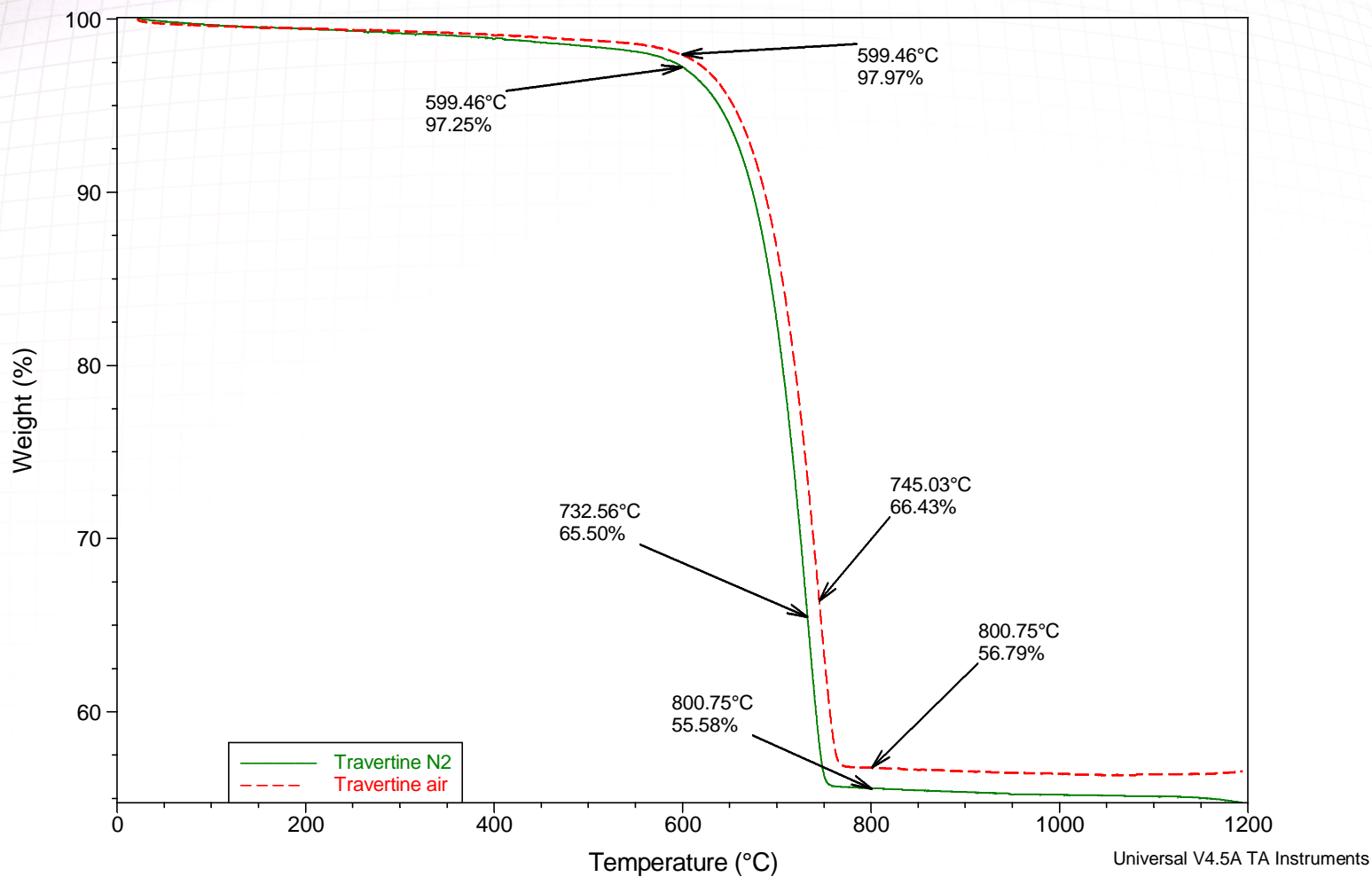


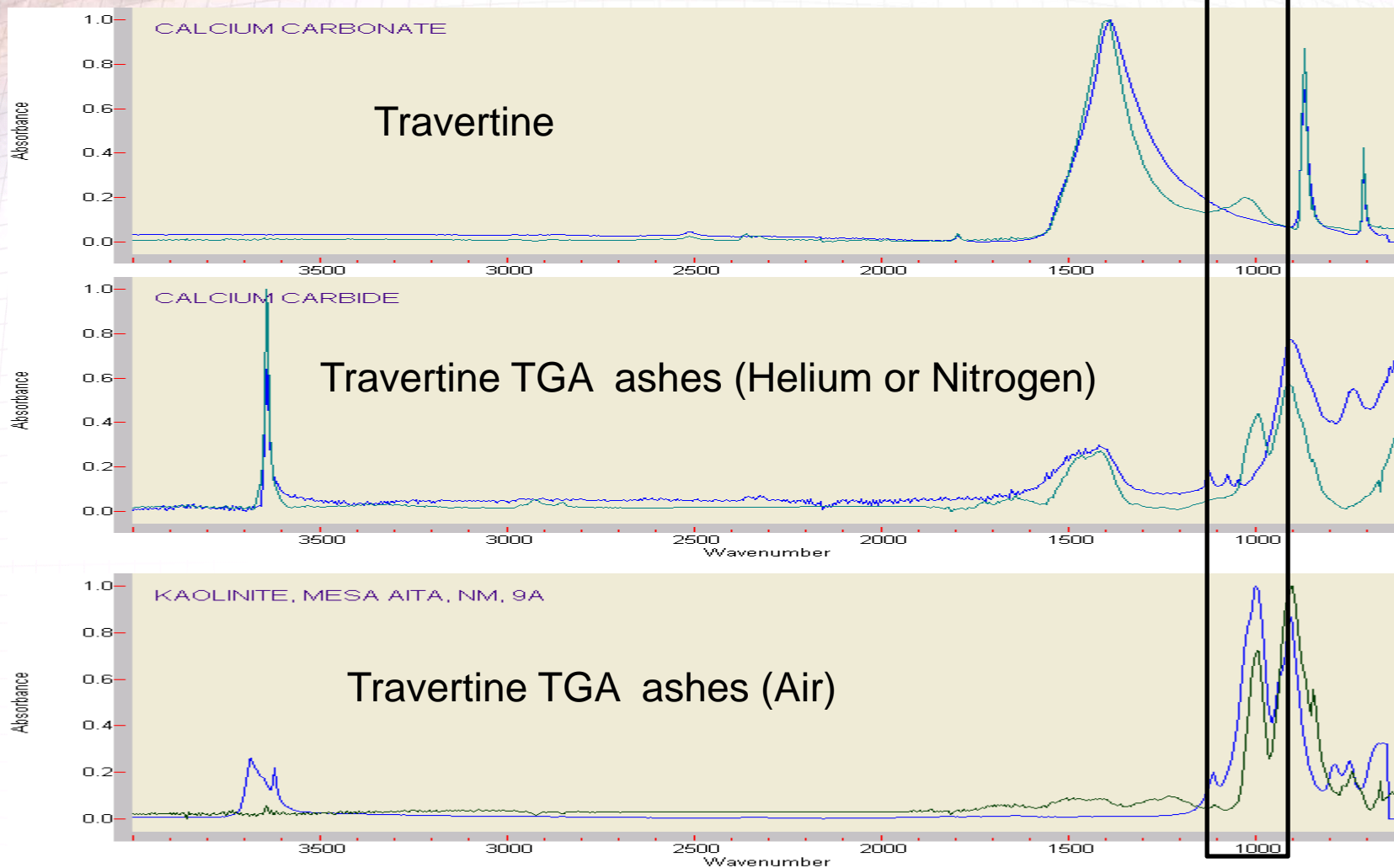
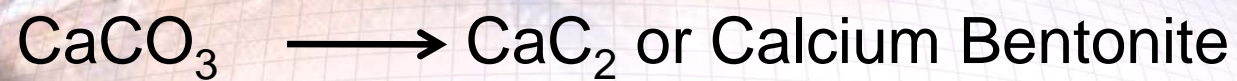
Brayco 815Z





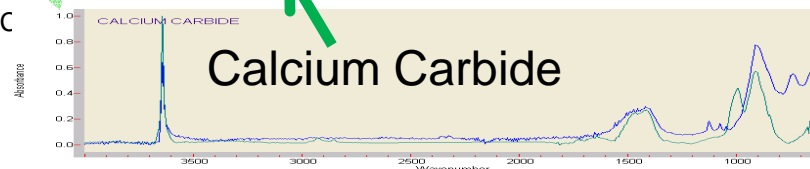
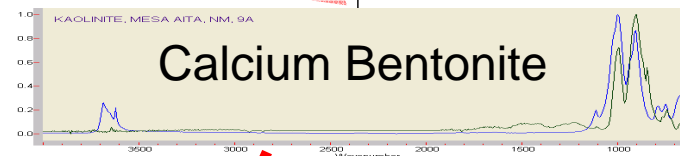
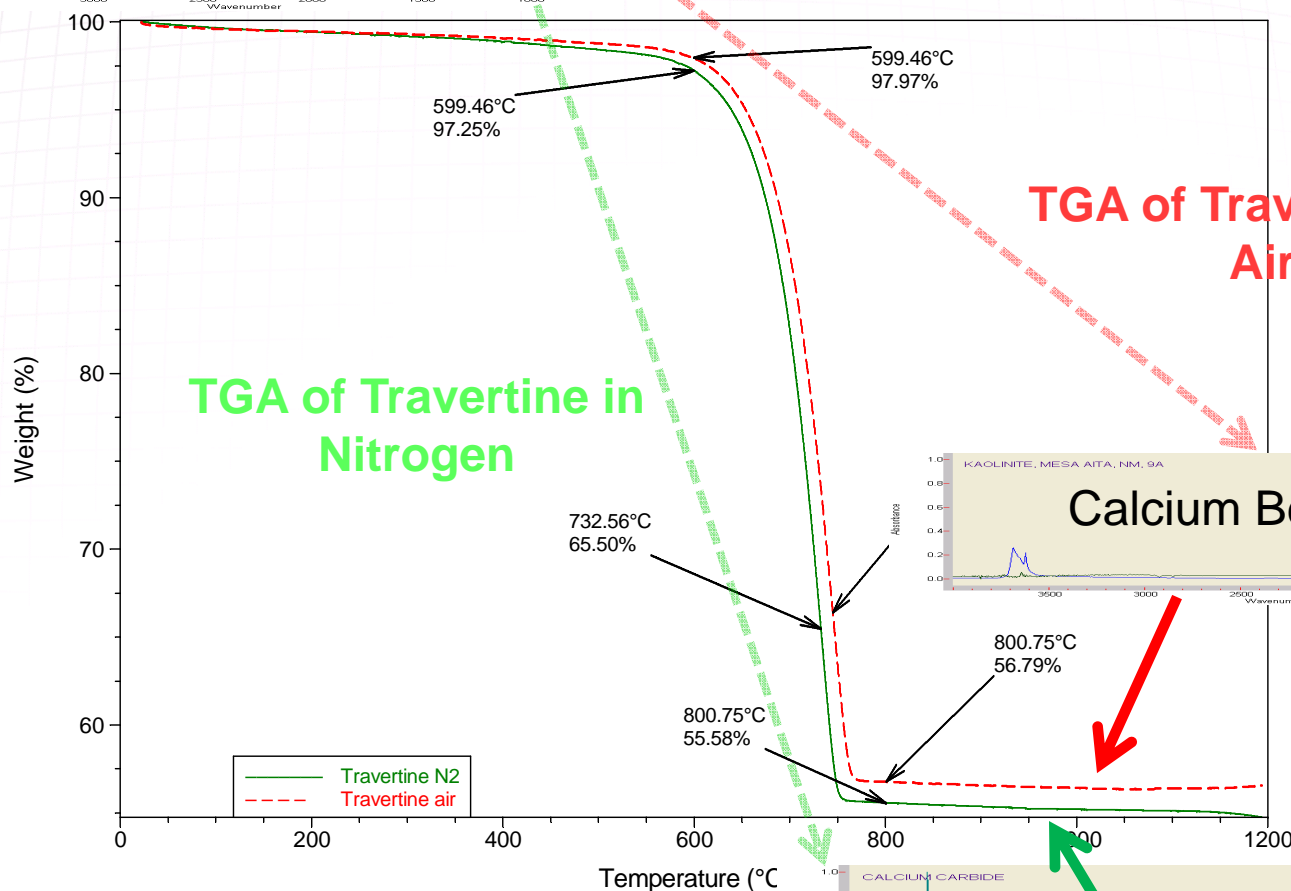
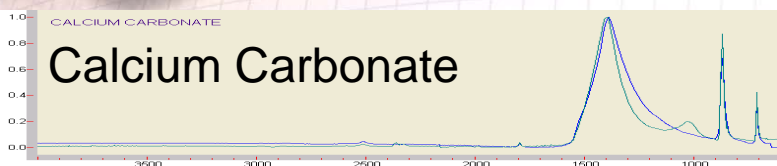
Thermal Response of Travertine in Different Atmospheres





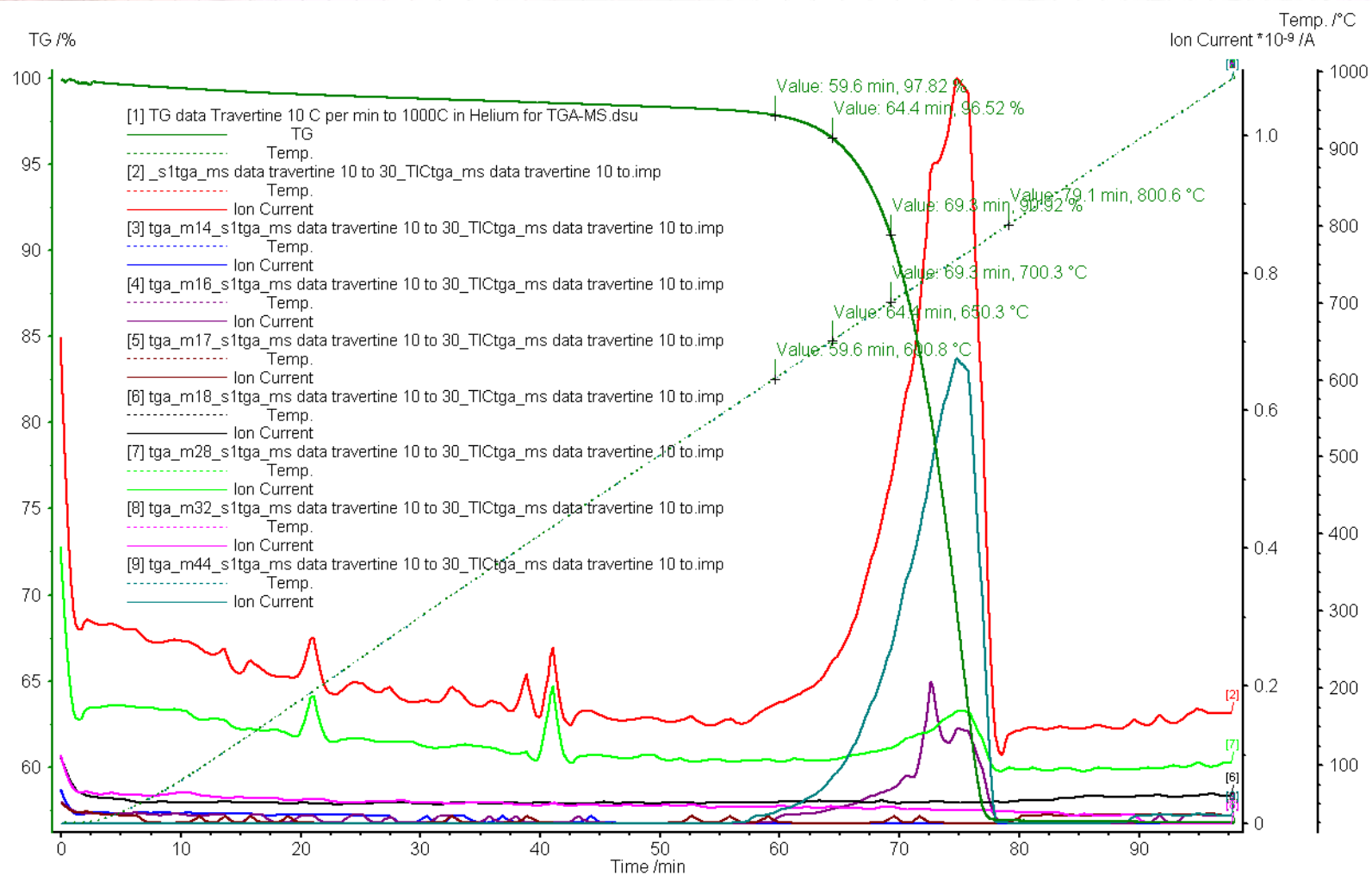


The Role of Gaseous Atmosphere During Thermal Decomposition of Travertine





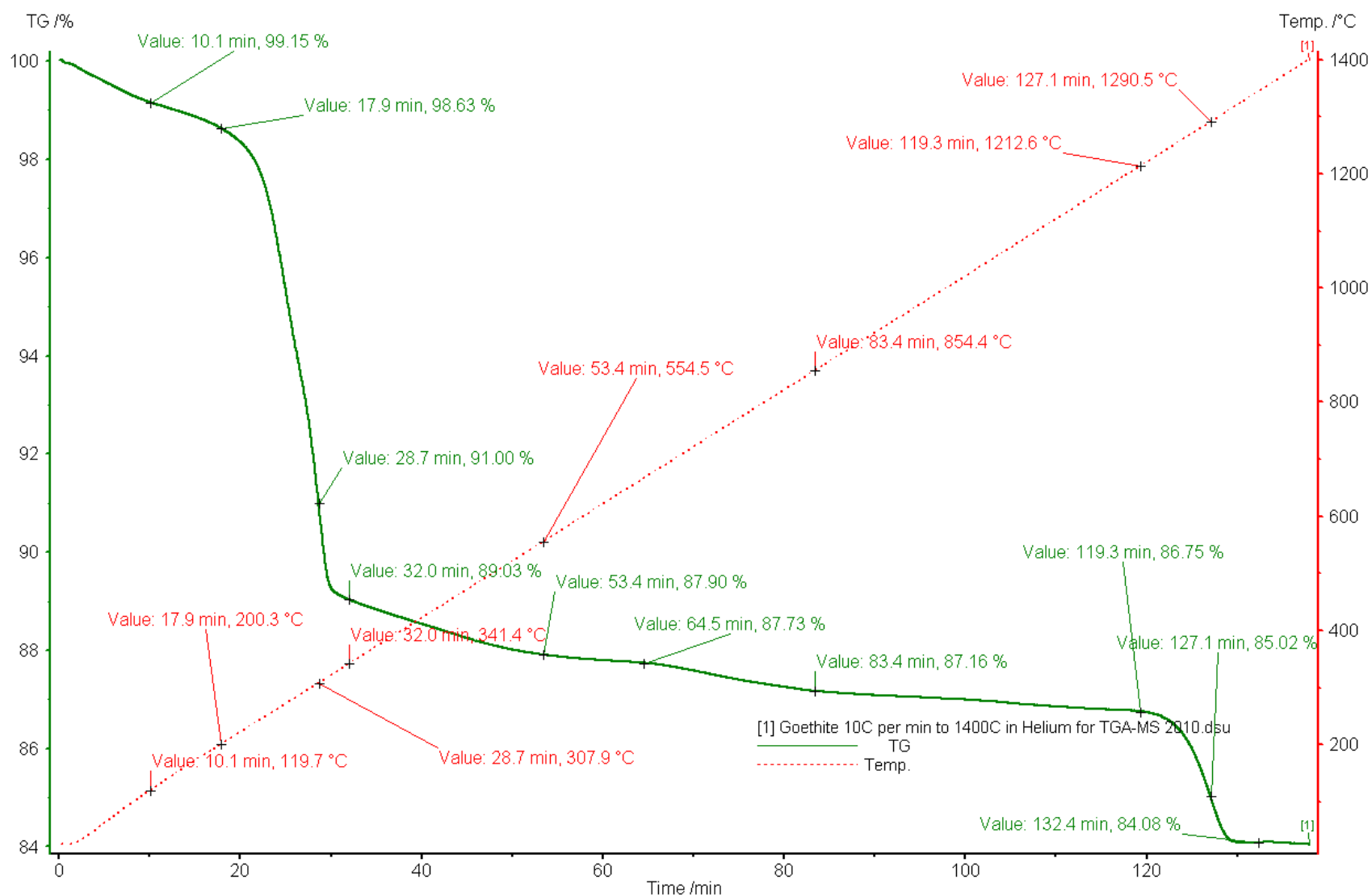
TGA-MS Analysis of Travertine



Substances being measured during mass loss near 700°C include CO₂, CO, and O[•]

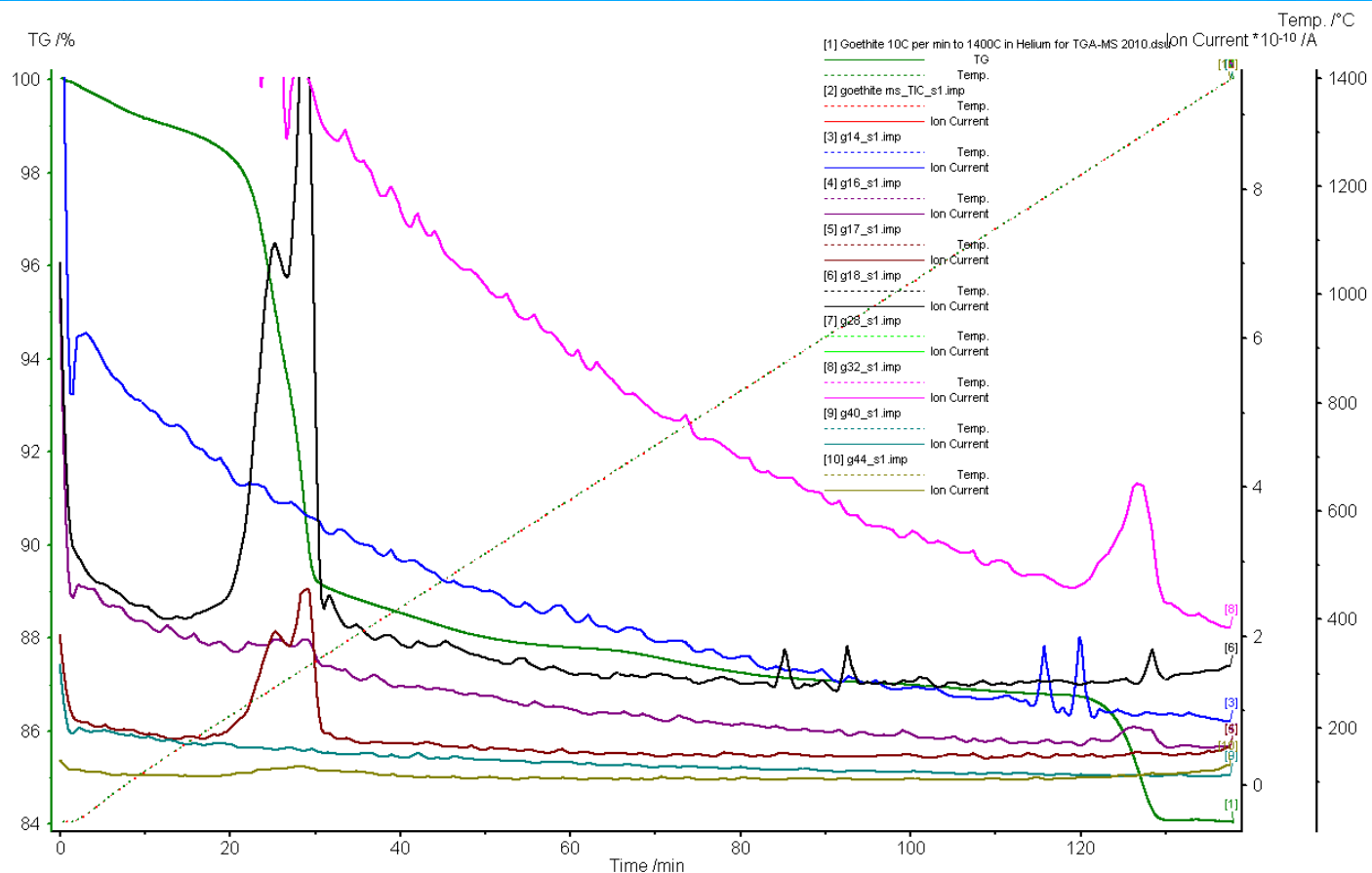


TGA Analysis of Geothite in Helium





Detected Mass Losses of Goethite



Goethite
 $\alpha\text{-FeO(OH)}$

At 120 $^{\circ}\text{C}$, Mass losses include:
 m/z 14 (CH_2), 16 (O), 32 (O_2)

At 308 $^{\circ}\text{C}$, Mass losses include:
 m/z 17 (OH), 18 (H_2O), 32 (O_2)

At 1290 $^{\circ}\text{C}$, Mass losses include:
 m/z 16 (O), 18 (H_2O), 32 (O_2)

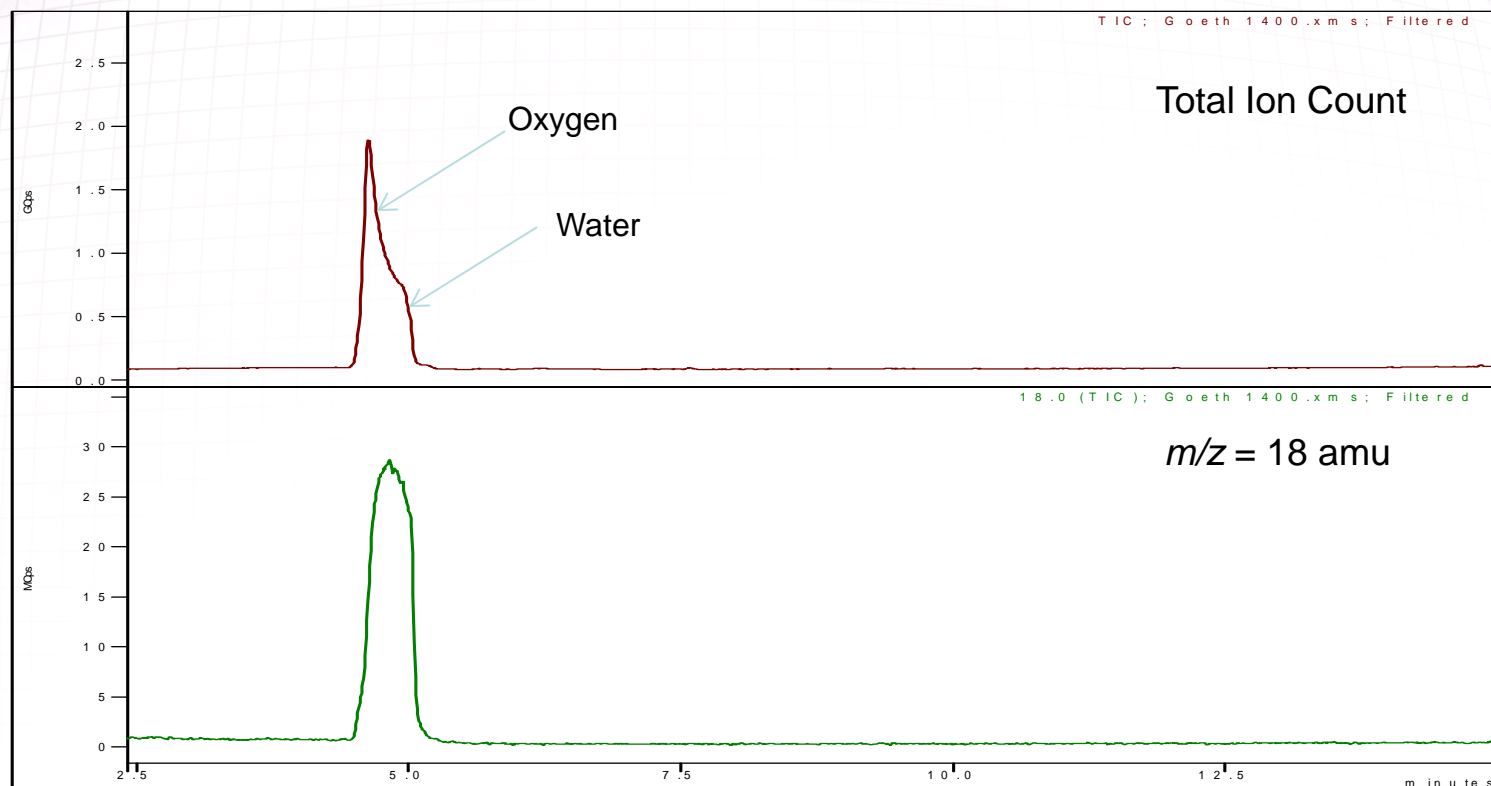


Goethite Analysis by Py-GC-MS at 1400°C

Chromatogram Plots

File: c:\brukerws\data\goeth 1400.xms
Sample: Goeth 1400
Scan Range: 1 - 3404 Time Range: 1.20 - 30.00 min.

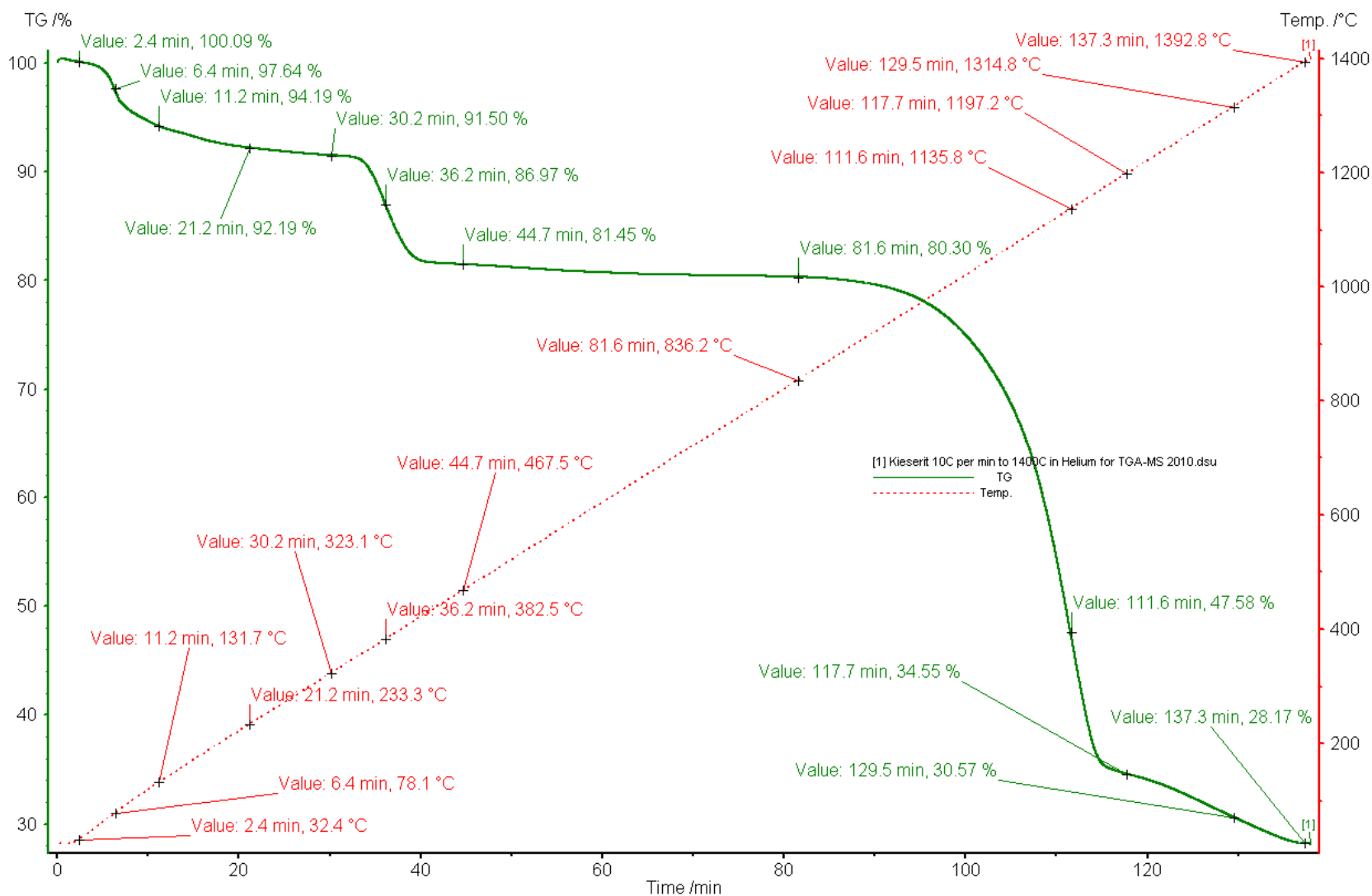
Operator: R Devivar
Date: 1/27/2014 4:49 PM



A sample of Goethite was first pyrolyzed at 750°C to remove all but the pertinent species. The same sample was then pyrolyzed at 1400°C

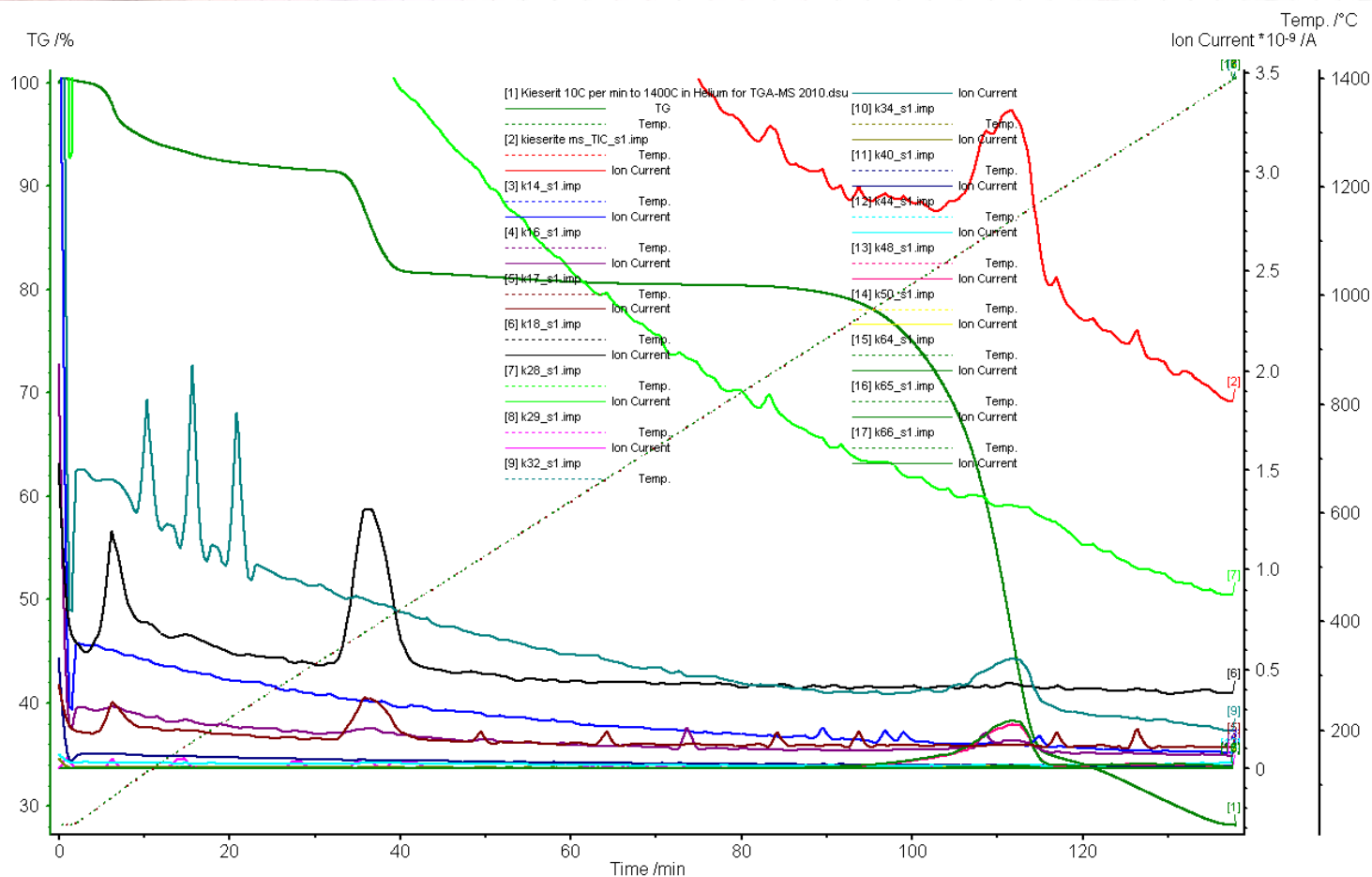


TGA Analysis of Kieserite





Detected Mass Losses of Kieserite



Kieserite
MgSO4·H2O

At 78°C, Mass losses include: m/z 17 (OH), 18 (H_2O), 28 (CO)

At 382°C, Mass losses include: m/z 16 (O), 17 (OH), 18 (H_2O), 28 (CO)

At 1136°C, Mass losses include: m/z 16 (O), 28 (CO), 32 (O_2), 48 (SO), and 64 (SO_2)

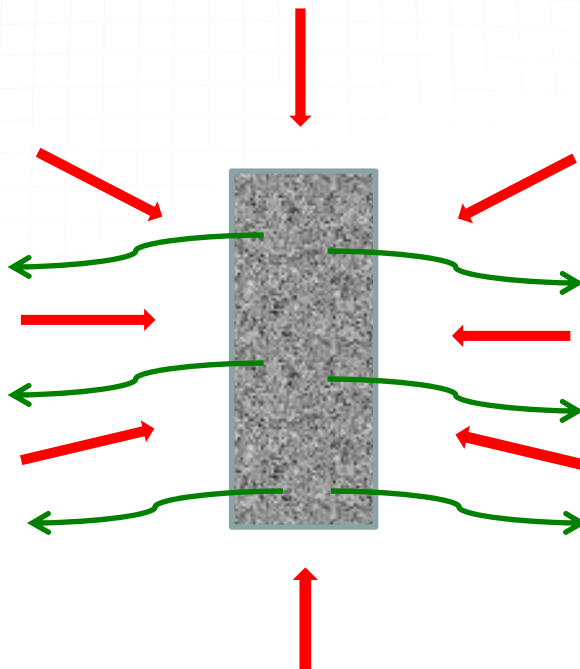
At 1315°C, Mass losses include: m/z 17 (OH), 48 (SO), and 64 (SO_2)



Applying Thermal Energy to Extract Chemical Information

Using Thermal Energy:

- How much Thermal Energy do we add
- How fast do we add the Thermal Energy
- How long do we maintain the Thermal Energy
- What atmosphere do we use
- How much sample do we use



Chemical Information

- Trapped solvent
- Organic additives
- Contaminants
- Labile Functional Groups
- Monomer identification
- Off-gassing information
- Inorganic additives

TGA

Pyrolysis-GC-MS

TGA-MS-IR